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Chemical  
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# **RENEWABLE ENERGY**

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### **CHEMICAL PROCESSING OF VEGETABLE OIL FUELS TO PREVENT POLYMERIZATION**

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Chemical processing of vegetable oil fue



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Chemical Processing of Vegetable Oil Fuels  
to Prevent Polymerization

Grant Agreement RAE-84-1041

Dr. Warren P. Scarrah  
Department of Chemical Engineering  
Montana State University  
Bozeman, Montana 59717  
Phone: (406) 994-5926

Project Location: Montana State University, Bozeman, Montana

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Project Scope: This was a research project using biomass as an energy source -- its purpose was to convert vegetable oil into a diesel fuel that would not polymerize when mixed with engine lubricating oil. The thermal decarboxylation and catalytic decarboxylation of safflower soap produced a satisfactory fuel. Other processes investigated that resulted in products that polymerized excessively included the thermal decarboxylation, catalytic decarboxylation, and hydrotreating of safflower oil. Hydrogenation of vegetable oil feedstocks and the resulting products was unsuccessful in that it turned the fuels into solids.



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# ABSTRACT

The purpose of this project was to determine how to produce diesel fuel from vegetable oils that would not cause polymerization when mixed with engine lubricating oil. A number of processes were investigated: the thermal and catalytic decarboxylation of safflower oil, the thermal and catalytic decarboxylation of safflower oil soap, and the hydrotreating of safflower oil. The safflower soap products had satisfactory polymerization properties with automotive lube oil; among the unsatisfactory products those from hydrotreating were superior to those from the decarboxylation of the safflower oil. Carboxyl (acid) groups or esters were present in the products that failed -- these groups appear to promote polymerization more than unsaturation (double bonds between adjacent carbon atoms). Hydrogenation at different stages resulted in products that were solid at ambient conditions rather than desirable liquid fuels. Probably because of the difference in additives between automotive and railroad lube oils, the safflower soap products did polymerize when mixed with the railroad lubricants.

## INTRODUCTION

Worldwide research is presently addressing the use of vegetable oils for diesel fuels. These fuels can consist of either the raw vegetable oil or various derivatives of that oil. Crude fuels were produced from many plant and animal oils during the first half of the 20th century. Uncertainty over supplies of petroleum-derived fuels is sparking new interest in vegetable substitutes.

Diesel fuels derived from vegetable oils are attractive alternatives for agricultural machinery. It should be possible for a farmer to plant a fraction of his land in oil-producing crops and use the fuel derived to power his entire operation. It has been estimated that about 10 percent of the cropland would be required to supply the fuel required to raise crops on the remaining 90 percent. As an added benefit, vegetable oil processing yields a high protein meal by-product suitable for animal feed.

Two principal problems have been identified with using vegetable oils directly as diesel fuels: (1) vegetable oils form carbon deposits inside direct injection engines and (2) vegetable oils carried into the crankcase polymerize with the lubricating oil leading to eventual engine failure. Both problems are related to the differences in chemical structure between vegetable oils and diesel fuel.

Vegetable oils are esters formed by the combination of glycerol with three fatty acids. These fatty acids are straight-chained, monocarboxylic acids that can be either saturated or unsaturated. It has been found that the carbon deposits can be avoided by either using indirect injection engines or by transesterification. Transesterification replaces one large triglyceride ester with three smaller esters. The principal change in physical characteristics of the transesterified vegetable oils is a significant reduction in viscosity compared to unmodified vegetable oils. This lower viscosity appears to prevent the formation of carbon deposits.

Transesterification, however, does not reduce the polymerization problem. Polymerization results from bonding with either the carbon double bonds or the carboxyl groups (both present in all crude vegetable oils). The high unsaturation level of the unprocessed oil has been reported to be the most likely cause, which transesterification does not eliminate. As the oil polymerizes, the lubricating properties of engine oil are destroyed and/or gums are formed which plug filters and lines.

Therefore, polymerization problems can presumably be solved by modifying the chemical structure of the vegetable oils to eliminate unsaturated carbon bonds and the carboxyl groups. The carbon double bonds can be removed relatively easily by hydrogenation but this results in a product that is unsuitable for fuel because



it is solid at room temperature. Decarboxylation (the removal of the carboxyl group from the fatty acid component) could be accomplished by thermal means with or without the aid of catalysts; the process used to accomplish decarboxylation is often referred to as thermal cracking or pyrolysis. Decarboxylation with subsequent hydrogenation would result in straight-chain, saturated hydrocarbon products with essentially the same chemical structure as the primary constituents of diesel fuel.

It is clear that vegetable oils require chemical modification before they are suitable for use as diesel fuels. It is doubtful that vegetable oil could be refined into diesel fuel on the farm. Even though decarboxylation and hydrogenation are relatively simple processes, they do involve high temperatures and pressures and it is not reasonable to expect that they can be successfully applied on a small-scale basis using part-time personnel. Decarboxylation and hydrogenation of vegetable oils would only be viable if done in a commercial processing facility using efficient technology. Identification of economical processes with moderate operating conditions is desirable.

This project explored methods for eliminating polymerization problems with vegetable oil fuel. The necessary tasks were divided into four sections or milestones:

1. Literature search and experimental plan
2. Hydrogenation, saponification, and thermal decarboxylation
3. Catalytic decarboxylation
4. Hydrotreating

This report presents the research objectives for each milestone, an outline of the experimental procedures used, a discussion of the results of each milestone, and a presentation of conclusions and recommendations.



## RESEARCH OBJECTIVES

The objectives for each of the milestones as outlined at the beginning of the project were:

### Milestone 1. Literature Search and Experimental Plan

1. The results of previous research on the uses of natural and modified vegetable oils for fuels will be summarized and evaluated to identify pertinent areas that merit further investigation.
2. Experimental designs will be prepared outlining the tests necessary to accomplish Milestones 2-4.

### Milestone 2. Hydrogenation, Saponification, and Thermal Decarboxylation

1. The relative importance of hydrogenation and thermal decarboxylation in preventing polymerization will be assessed for vegetable oils.
2. The effect of hydrogenation of vegetable oils and soaps before thermal decarboxylation on product yields and polymerization properties will be determined.
3. The necessity for hydrogenation of products after decarboxylation to prevent polymerization will be evaluated.

### Milestone 3. Catalytic Decarboxylation

1. It will be determined if the catalytic decarboxylation of vegetable oils using alkali metal hydroxides and the thermal decarboxylation of soaps produce equivalent diesel fuels.
2. The effect of converting a vegetable oil to a soap prior to catalytic decarboxylation with the corresponding alkali metal hydroxide will be evaluated relative to product yields and polymerization properties.
3. The effect of the hydrogenation of vegetable oils and soaps before catalytic decarboxylation on product yields and polymerization properties will be determined.
4. The necessity for the hydrogenation of products after catalytic decarboxylation to prevent product polymerization will be evaluated.

### Milestone 4. Hydrotreating

1. The effects of process variables on the product iodine values (a measure of the unsaturation of carbon bonds) will be determined for the hydrotreating of vegetable oils.
2. For the most promising hydrotreating processing conditions, the effect of hydrotreating on product yields and polymerization properties will be determined.



## EXPERIMENTAL DESCRIPTION

### 1. Raw Materials

Safflower mill oil, refined in Montana, was selected as the primary vegetable oil feedstock for these experiments. Safflower oil was chosen because it is an important Montana oilseed crop and also because of its availability. Further, safflower and sunflower oils, which are chemically similar, have both been the subjects of extensive fuels research.

Rapeseed oil, which is also produced from plants grown extensively in Montana, was to have been used to verify the results obtained with the safflower oil. The safflower experiments with the highest yields and best results were to have been duplicated using rapeseed oil. Rapeseed oil was chosen for the same reasons as the safflower oil. Although the rapeseed oil experiments were performed, subsequent analysis of the rapeseed oil by a commercial laboratory indicated something was wrong with it -- only about half of the sample consisted of the fatty acid components typical of vegetable oils or animal fats (it had somehow been contaminated with what smelled like petroleum-derived solvents). Therefore, most experimental data collected using the spurious rapeseed oil will not be presented or discussed in this report. Some polymerization data will be discussed, however, to generalize on the effects of vegetable oil fuel mixed with lubricating oils.

Two base lubricating oils were used to determine thickening properties. Most runs were made using Phillips 66 Super HD II SAE 30W and other runs made with Burlington Northern Specification # 13 TBN SAE 45.

### 2. Procedures

#### Hydrogenation

Hydrogenation of the raw safflower oil and other materials was done in a Parr Instrument Co. series 4000 pressure reaction apparatus. This equipment consisted of a 500 ml stainless steel bomb, rocker assembly, thermocouple, pressure gauge, hydrogen tank, pressure lines, and valves. A Pyrex glass liner was used inside the bomb to keep the bomb clean and to prevent the metal from possibly catalyzing the reaction. Between 100 and 150 ml of raw oil was processed at a time in a batch reaction.

Two different hydrogenation catalysts were used. For the first few runs, a Harshaw nickel catalyst (Ni-1430, E 1/8) was used. This catalyst turned out to be very ineffective at the required operating conditions and was replaced with a Raney nickel catalyst (42% Ni, 58% Al) from W.R. Grace & Co. The Raney nickel proved to be an active hydrogenation catalyst and was subsequently used to produce most of the saturated oil. The Harshaw catalyst could be used without modification but the Raney nickel required a



preparation procedure to activate it. A method outlined in the Journal of the American Chemical Society was slightly modified to prepare the Raney Nickel. This procedure consisted of leaching out the aluminum with a 20 percent sodium hydroxide solution for about one hour. The catalyst particles were then washed with distilled water to remove all traces of sodium hydroxide. Washing with ethanol removed the water and the catalyst was dried and immediately stored under oil. The final product, a pure, high-surface-area nickel, was subject to rapid deactivation with time or exposure to air.

Hydrogenation reaction conditions were based on standard industrial operating procedures for edible vegetable oils and fatty acids. Since a batch system was used, the approximate degree of hydrogenation was calculated from the decrease in the bomb hydrogen pressure. Initial hydrogen pressure was varied between 150 and 1500 psig. After the first few experiments, pressures of 1500 psig were used exclusively. The system was re-pressurized to 1500 psig periodically following pressure drops caused by hydrogen consumption. Reaction temperatures averaged 300 F and did not exceed 350 F because decomposition or discoloration was reported to take place at temperatures near 400 F. The reaction time varied between two and ten hours depending on the catalyst used, the degree of hydrogenation required, and the average hydrogen pressure.

After the hydrogenation rate substantially decreased, the reaction bomb was allowed to cool. Later the solid product was liquefied and filtered to remove the catalyst. Rather than trying to characterize each product separately, a uniform material was made by combining the products from all the hydrogenation experiments.

Once a general hydrogenation procedure was established, pressure and temperature data were recorded only as often as necessary to monitor the extent of the reaction and to assure that oil decomposition did not occur.

#### Saponification

Saponification reactions were performed in 500 ml glass batch reactor at atmospheric pressure with a water-cooled condenser. About 200 grams of raw vegetable oil was reacted with at least 50 percent excess of the stoichiometric amount of sodium hydroxide solution. For saponification, thermal decarboxylation, and catalytic decarboxylation, a combination heating mantle-magnetic stirrer was used to heat the reactor while simultaneously mixing it with a stirring bar. This mixture was kept at its boiling temperature until the reaction appeared complete. The sodium soap was separated from the mixture by dissolving in hot water. A solution of calcium chloride was then added to replace the sodium ions with calcium which precipitated the soap. The resulting calcium soaps were filtered, washed, and dried for use in subsequent experiments.



Hydrogenated soaps were made by saponifying partially saturated oils by the above procedure. This sequence was used rather than trying to hydrogenate unsaturated soaps because of reports of catalyst poisoning by the soaps.

#### Thermal Decarboxylation

Decarboxylation reactions were also performed in a glass batch reactor having an atmospheric Liebig-type distilling head to condense the resulting products; both liquid and vapor temperatures were measured.

The quantity of reactants used in the decarboxylation reactions was 150 grams of the raw vegetable oil and varying amounts of the soap. The amount of soap used in each reaction was kept as constant as possible. This was difficult due to the highly variable water contents of the raw soaps.

Heat was continually supplied to the various decarboxylation experiments to keep the liquid distillate rate fairly high. The reaction was considered complete when no further liquid could be distilled from the reaction mixture at reasonable temperatures or when the condenser became completely plugged with solid products.

#### Catalytic Decarboxylation

The catalytic decarboxylation procedure was essentially the same as the thermal decarboxylation procedure described above. The amount of catalyst added to the reactor varied from 3 g to 15 g. The vigorous stirring provided by the magnetic stirrer reduced mass transfer resistance between the catalyst surface and the reactants or products to the point where the quantity of catalyst was not a significant variable. This was verified by the results of four pairs of duplicate experiments in which each experiment in a given pair differed only by the amount of catalyst used -- product yields and properties were essentially the same for both experiments in each pair.

#### Hydrotreating

The same apparatus and general operating procedures described above for hydrogenation were used for the hydrotreating experiments. However, only small quantities of vegetable oil (3-7 ml) could be used for each experiment because it was desirable to maintain a constant ratio of hydrogen to vegetable oil; this ratio was set at a value typically used to hydrotreat petroleum feedstocks, 10,000 SCF (standard cubic feet) of hydrogen per barrel (42 gal) of oil. A relatively high catalyst concentration was used - 2.65 wt% of the oil. It took one to two hours to heat the reaction bomb to the desired temperature at which it was held for 30 minutes; the heater and rocking mechanism were then turned off and the bomb allowed to cool.



Some procedure alterations had to be made to provide enough product for a distillation characterization and polymerization test. After determining which variable values gave the best product from the tests described above, five additional hydro-treating runs were made using that particular temperature, pressure, and catalyst. However, to produce enough product in a reasonable amount of runs the amount of vegetable oil was significantly increased for each run and resulted in a ratio of about 2,000-3,000 SCF of hydrogen per barrel of vegetable oil.

#### Polymerization

The polymerization reactions were carried out in a glass batch reactor using approximately 500 ml of the desired lubricating oil as the base stock. The product to be evaluated was mixed with this base stock to make a 5 percent solution.

The purpose of the polymerization experiments was to simulate crankcase oil conditions in a diesel engine and to determine the thickening effects of adding 5 percent of the proposed fuel substitute to the engine lubricating oil. To accomplish this, the experiments were run for 60 or 70 hours at a constant temperature of 150 C. Pure oxygen was bubbled through the oil mixture at a rate of approximately 2 ml/sec. A 20 cm<sup>2</sup> strip of copper was used as a catalyst. The kinematic viscosity at 40 C was measured every ten hours and plotted to show thickening characteristics versus time. According to one source, a similar test was considered a success if the oil had less than a 375 percent increase in kinematic viscosity in 64 hours.

#### 3. Analytical

Numerous tests were performed to characterize the various feed materials and products formed in this research project. They included: iodine value, kinematic viscosity, moisture content, density, distillation ranges, and acid number. In the interest of consistency and reproducibility of results, a standard U.S. Government ASTM test procedure was used whenever possible. Some of these same tests are part of the standard specification for diesel fuel oils - ASTM D 975-81. Thus it was felt that results from these tests in combination with the polymerization data would give a good indication how the decarboxylation products would perform as fuels. Some of the physical properties for diesel fuel from this specification are:

Distillation Temperature (90% point)  
Maximum - 640 F  
Kinematic Viscosity, cSt, 40 C  
Minimum - 1.9  
Maximum - 4.1

The iodine value of an oil is the measure of its unsaturation, i.e., relative number of carbon-carbon double bonds. The



method used to measure iodine values was the common Wijs Procedure performed according to ASTM D 1959-69. This method has been shown to give accurate results for oils with nonconjugated double bonds. These are the only type present in crude safflower and rapeseed oils and their derivatives. Iodine value is expressed as centigrams of iodine absorbed per gram of sample. If the average molecular weight of the sample and its iodine value are known, the average number of double bonds per molecule can be calculated.

The kinematic viscosities of all liquid polymerization and decarboxylation products were measured using the Cannon-Fenske Routine. These tests were all run at a constant temperature of 40 C per ASTM D 445-79. However, when investigating the effects of process variables during the hydrotreating tests, it was necessary to make a visual comparison of viscosities. There was so little product available from each test that a kinematic viscosity could not be determined; therefore, the products were placed in glass vials and their flow characteristics (viscosities) qualitatively compared to the raw safflower oil. The products were rated relative to the safflower oil as having viscosities appearing lower, equal to, slightly higher, or higher.

Moisture contents of all feed materials were measured using the distillation procedure detailed in ASTM D 460-78. The soap or oil was refluxed with toluene and the water collected in a trap after condensing.

Densities of all liquid decarboxylation products at 20 C were calculated by weighing and measuring their volume in a graduated cylinder.

The purpose of the distillation tests was to determine the volatility characteristics of the various decarboxylation products. The method used is similar to that specified in ASTM D86-78. It differs in the fact that the distillation is considered complete at 640 F since this is the approximate end point given for diesel fuel in this standard. The liquid distilling above 640 F is considered to be residue. The apparatus used in this experiment included a boiling flask with a vapor temperature thermometer, condenser, and receiving flask.

The acid number of an oil or oil product is a relative measure of the free fatty acid content. The procedure used is that described in ASTM D 460-78. This involves dissolving the oil in hot 95 percent ethanol and titrating with KOH to a phenolphthalein end point. Acid number is expressed as centigrams of KOH per gram of sample.



## RESULTS AND DISCUSSION

### Milestone 1. Literature Search and Experimental Plan

The value of the comprehensive literature search was that it identified subject areas that should be investigated. Even though the initial research proposal had been based on sound information, it did not have the perspective that was later gained by the more thorough evaluation of the previous research. The literature search indicated that a more valuable project would result if several modifications were made to the milestones initially proposed. A brief overview of the results of the literature survey is followed by a discussion of how the experimental plan was modified in light of this information. A comprehensive discussion of the literature search is included in the Appendix.

There were two active periods of research addressing the conversion of vegetable oils into fuels: (1) the early period between 1888 and 1951 and (2) the current period. The early period experiments gave some data that was questionable, and it was difficult to compare product yields because many different calculation methods were used. Little research was done in this field from the early 1950's until the late 1970's due to the availability of inexpensive petroleum. The review of current research extends from 1978 through 1983. Although both decarboxylation and hydrogenation are important in the production of diesel fuels, it was found that very little information was available concerning the effects of hydrogenation on vegetable oils. Therefore, the review primarily addresses decarboxylation with only a few references related to hydrogenation.

Four decarboxylation processes were identified. The liquid-phase catalytic process and the soap pyrolysis had definite advantages over both the vapor-phase cracking and liquid-phase pressure cracking. They allowed processing at lower temperatures and pressures which would be beneficial both in terms of equipment and operating costs and, of course, safety. The most important factor, however, was that these two processes had been shown to consistently give higher yields of diesel-range products than the other two methods.

The value of vegetable oil hydrogenation was inferred by comparing the characteristics of the fuels produced from vegetable oils with different amounts of saturation. According to the data, the degree of unsaturation of the raw vegetable oil used had an effect on the quantity and type of products formed, no matter which decarboxylation process was used. Decarboxylation of saturated oils produced more liquid products (less gaseous and solid), and the products that were formed had a higher average molecular weight (more diesel range products) than unsaturated oils. The exact reason for this is unknown, but seems to have something to do with the decarboxylation mechanisms which change with increasing unsaturation. Lighter products were apparently formed as the oils



"cracked" at the double bonds rather than at the carboxyl groups. This area was not explored by many researchers because they were usually attempting to maximize the gasoline-range products and the extra cracking was desirable.

The literature search resulted in a significant decrease in emphasis on investigating the effects of process variables on the hydrogenation of vegetable oils -- this appeared to be a fairly straightforward process. It was also apparent that, if vegetable oils were to be modified prior to being converted to fuel, it was preferable to change them into soaps rather than fatty acids or smaller esters (transesterification). Catalytic decarboxylation had given better yields of diesel-range product than thermal decarboxylation, so it was decided to expand the investigation of the former process and reduce that of the latter. Hydrotreating was also added to the processes to be examined -- it is a combination of hydrogenation and catalytic cracking and both appeared to be beneficial for the production of diesel fuel.

#### Milestone 2. Hydrogenation, Saponification, and Thermal Decarboxylation

This portion of the research was concerned with saturating raw safflower oil, safflower soaps, and certain decarboxylation products. However, hydrogenation was not analyzed in detail and only pertinent results are reported.

The effects of changes in temperature and pressure on the reaction rate were not studied extensively, but general trends were noted. As expected, it was found that the hydrogenation rate increased with increasing hydrogen pressure. At 1500 psig the time required for reaction was substantially less than at 150 psig.

As previously stated, decarboxylation of highly saturated vegetable oils was reported to give higher liquid product yields than decarboxylation of comparable unsaturated oils. Therefore, some safflower oil and safflower soaps were partially saturated prior to the decarboxylation process. The crude safflower was hydrogenated from an iodine value of 149 down to an average value of 37. At this level of saturation the product was a hard white solid at room temperature. Decomposition of these hydrogenated materials, however, resulted exclusively in solid products at room temperature. The condenser became plugged with these solids which forced the end of the experiment. Because these products were solids at room temperature they would be poor fuel substitutes. Therefore, the products were not characterized and no polymerization studies were performed on them. Hydrocracking of these vegetable oils might combine hydrogenation and decarboxylation and result in better liquid product yields. Hydrocracking involves high temperatures in conjunction with high hydrogen pressures and was briefly be investigated during Milestone 4 of this project.



Hydrogenation was also performed on a select few of the decarboxylation products. These included products from the thermal decomposition of safflower and rapeseed oils and soaps. They were all hydrogenated quite extensively and all turned solid at the resultant low iodine values. These hydrogenated decarboxylation products were solids at room temperature, which would make them unacceptable as fuel substitutes. Therefore, no polymerization tests were performed on them.

#### Saponification

Because it was not the primary research objective, saponification of vegetable oils was not examined in detail. Some details about saponification which were not found in the literature were discovered by experimentation and are given below. Hereafter, unless otherwise specified, all soaps mentioned are calcium soaps.

A solution of approximately 25 percent sodium hydroxide (NaOH) seemed to give a faster reaction rate than much weaker or stronger concentrations. Refluxing the reaction mixture at its boiling point was more effective than trying to keep the solution just below the boiling point to prevent boil over. It took two to three hours for completion of the reaction using 50-100 percent excess NaOH. The calcium soaps produced by ion exchange were insoluble in water and easily separated from their soluble sodium counterparts.

Moisture content determinations were performed on safflower, hydrogenated safflower, and rapeseed soaps. In all cases it was found that the soap dried with aging. Moisture contents varied from as high as 47 percent for week-old soap to as low as 3 percent for month-old soap.

#### Thermal Decarboxylation

Decarboxylation was the primary objective of this research, but it was not successfully accomplished in all experiments. The majority of the products retained a fairly high concentration of carboxyl groups, in the form of fatty acids, even after high temperature processing. Some decarboxylation was evident in all experiments, however, and the term is used interchangeably with decomposition of the vegetable oils and their derivatives. Fatty acid content of the products was measured by titration with a base to obtain the acid number. Lower acid numbers indicated products which had been decarboxylated extensively, i.e., more hydrocarbons and fewer fatty acids.

Table 1 shows the detailed results from the successful thermal decarboxylation experiments. Yields for the oil products were calculated on a weight percent of the raw vegetable oil. The soap yields were determined on a water-free basis because of inconsistent moisture contents in the raw soap. Distillate, water, and bottoms percentages did not usually add up to 100 percent because



Table 1. Thermal Decarboxylation Results

Exp. No.	Form	Yields (wt%)		Max. Temp. (°F)	Distillate		
		Distillate	Water		Viscosity (cSt)	Iodine Value	Acid Number
1	Safflower Oil	35.5	1.6	725	2.85	92	226
2	Safflower Soap	10.1	-	700	4.44	90	175
4	Safflower Soap	27.9	-	745	-	152	2
8	Safflower Oil	68.5	1.5	825	4.50	101	170
24**	Safflower Oil	73.4	1.1	850	6.76	97	163
25**	Safflower Soap	55.6	-	800	3.33	160	5
31	Safflower Soap	47.0	-	930*	2.97	147	1

\* Flask temperature

\*\* Denotes that a polymerization study was performed on this product

some products were lost as uncondensable gases. Also, some material was lost due to small leaks and leftover residues in the equipment. An accurate bottoms yield was calculated on only one of the soap decarboxylation products (#30, Table 1). The residue following these soap reactions was invariably a black, solid mess, which made cleaning the glassware and subsequent calculation of residue yields difficult.

The liquid product yield for all decarboxylation reactions was dependent on the maximum temperature obtained. It was necessary to keep the reaction temperature relatively high to decompose the oils into lighter boiling compounds. Higher temperatures, however, caused heavier products to distill over. These heavier products usually raised the average boiling point and kinematic viscosity of the mixture above the range for No. 2 diesel fuel.

The maximum reaction temperature measured, as shown in Table 1, was not always consistent between experiments. Also, as the soap decarboxylation experiments neared completion, solid residues insulated the thermometer from the reaction vessel, and the resulting temperature readings were inaccurate. In many of the soap pyrolysis experiments, the Pyrex reaction vessel softened and, in a few cases, melted at temperatures registered by the thermometer of less than 900 F. Accurate temperature measurements were recorded during the vegetable oil decarboxylations because the reaction mixture remained liquid.

Thermal decarboxylation of raw safflower oil produced fairly high yields (up to 73 percent) of liquid products (SOTD). This product was selected for a polymerization study (#24, Table 1). The yield of liquid product from the thermal decarboxylation of safflower soaps (SSTD) was 56 percent - considerably lower than from the SOTD run. This SSTD product was chosen for polymerization studies (#25, Table 1).

The iodine values of the thermal decomposition products of safflower oil were in the neighborhood of 100; quite a bit lower than the original oil value of 149. The iodine values (around 150) for the liquid products from the safflower soaps were comparable to the value of the crude safflower oil.

The kinematic viscosity of the SOTD product was about an order of magnitude lower than the raw oil. Kinematic viscosities of safflower soap products were usually lower than that for the oil decomposition products. The liquid product yields were also lower, which would partially explain the lower viscosities. Decomposition of raw safflower oil to these same lower yields would also result in a lighter liquid product and its accompanying lower viscosity.

Distillation ranges were determined for all the thermal decarboxylation products selected for polymerization study, and are listed in Table 2.



Table 2. Distillation Characteristics of Thermal Decarboxylation Products

Product	Total Dist. (vol%)	Temperature (°F) at Volume Distilled										
		Initial	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%
SOTD	60	145	165	345	430	453	560	587	620	-	-	-
SSTD	76	176	263	295	365	423	470	525	588	635	-	-

Two thermal decarboxylation runs were made using soap produced from the material thought to be rapeseed oil. A polymerization study and distillation test were also made on the thermal decarboxylation products. Any experimental data obtained using the rapeseed oil is unreliable and has not been reported because the properties of the vegetable oil cannot be separated from those of the contaminating solvent. However, the results of polymerization tests of thermal decarboxylation products from rapeseed oil are discussed in the Milestone 3 section -- they have been included not to represent the properties of rapeseed oil fuels but to verify that vegetable oil fuels show different polymerization properties when mixed with automotive lube oil than when mixed with railroad lube oil.

#### Polymerization

The polymerization or thickening tests were designed to show the compatibility of the proposed diesel fuel substitute with crankcase oil at high temperatures in the presence of oxygen and a copper catalyst. Some of the decarboxylation products with viscosities similar to No. 2 diesel fuel were selected for these studies. The samples for polymerization study were taken from the entire decarboxylation product, not merely the portion in the diesel fuel range. Products with the highest yields in combination with the best physical properties were chosen from each of the following categories:

1. Safflower oil thermal decomposition (SOTD)
2. Safflower soap thermal decomposition (SSTD)

The results are plotted in Figure 1 as kinematic viscosity of the lube oil versus time. Also included is a baseline test done with crude safflower oil; the kinematic viscosity of the lube oil with 5 percent safflower oil increases exponentially with time.

The kinematic viscosity using the safflower oil product (SOTD) increased rapidly between 20 and 30 hours, and then the rate of thickening tapered off somewhat. A substantial quantity of very thick, semi-solid material was formed during the polymerization test of the SOTD product. This "sludge" was much thicker than the remaining oil, settled to the bottom of the vessel, and was not collected in the samples used for the viscosity tests. Also, the surface of the copper strip used in both of these tests was covered with a layer of hard black material. The presence of heavy "sludge" in the reaction vessel following polymerization tests was important. It probably caused the tapering off of the rapid viscosity rise in the graphs. The decarboxylation products were consumed to form "sludge", leaving fewer of them to polymerize with the remaining lube oil. Therefore, Figure 1 does not represent a true picture of overall viscosity changes with respect to time. This heavy material would also undoubtedly gum up an engine if these products were used as diesel fuels.



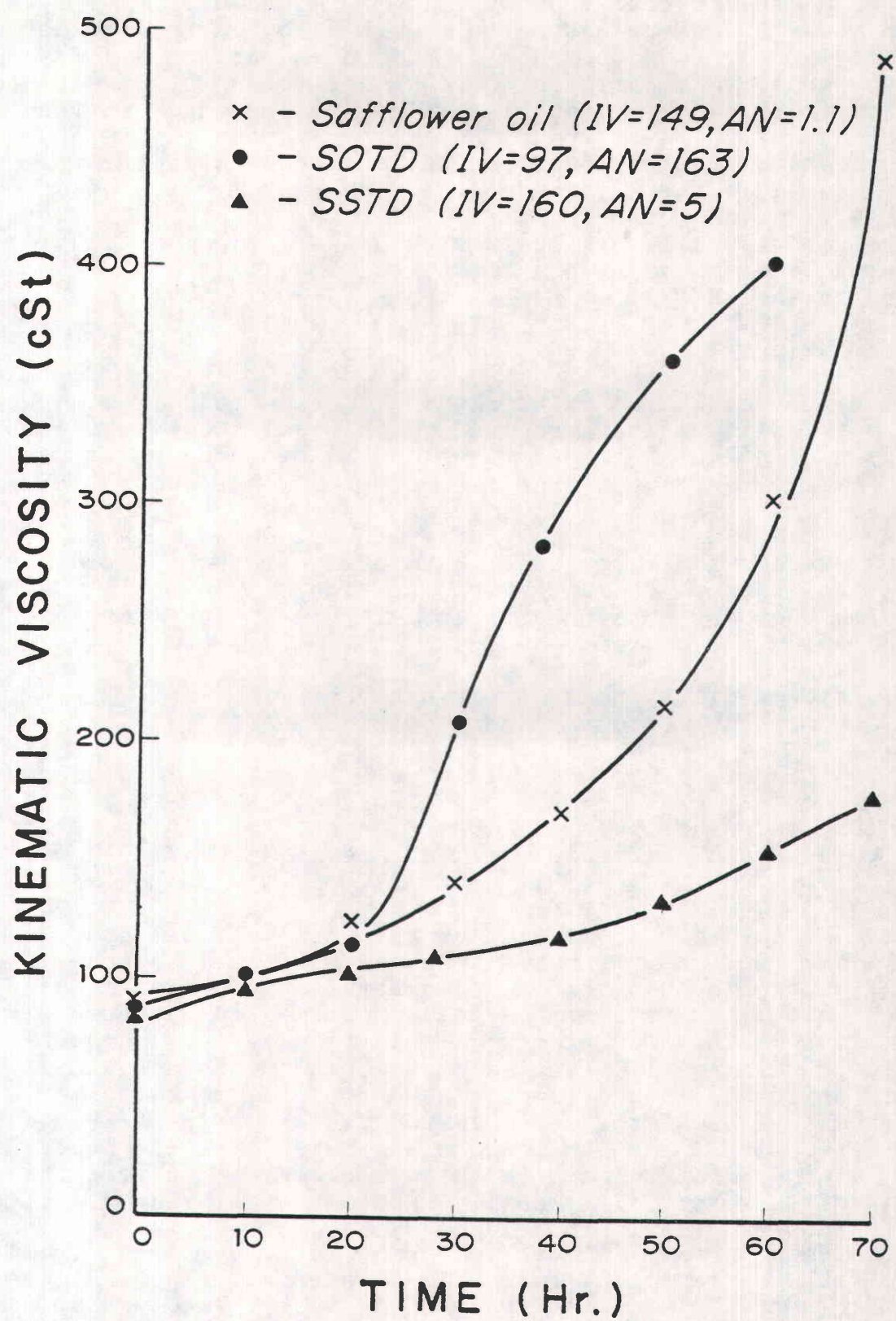


Figure 1. Polymerization Characteristics of Thermal Decarboxylation Products and Safflower Oil in Automotive Lube Oil



The thickening test results for the SSTD product showed a very slow rise of kinematic viscosity. Also no "sludge" was found in the reaction vessel and the surface of the copper strip was clean following the test.

Even though the safflower soap decarboxylation product had a significantly higher iodine value than the safflower oil decomposition product (160 compared to 97), it did not polymerize with the lube oil nearly as much. This seems to refute any theory which states that unsaturation is the only contributor to polymerization of lubricating oils. It is, however, certainly a factor because of the high reactivity of the double bond sites.

Other differences between the safflower oil and soap decarboxylation products were their acid numbers and kinematic viscosities. The SOTD product has a much higher acid number (163 vs. 5) and slightly higher viscosity (6.76 cSt vs. 3.33 cSt) than the SSTD product. Polymerization differences could be partly attributed to either of these properties.

It is possible that the carboxyl component of the fatty acid could lead to additional polymerization of the oil. This theory is supported by the fact that raw safflower oil, which is composed mostly of fatty acids in the form of carboxylates, polymerizes with lube oil extensively. Additional support for the theory that the presence of carboxyl groups is the dominating cause of polymerization was provided by carbon-13 nuclear magnetic resonance measurements ( $^{13}\text{C}$  NMR). These analyses were made on products from the thermal decomposition of safflower soap, from the catalytic decarboxylation of safflower oil, and from the hydrotreating of safflower oil (they are compared and discussed in the Milestone 3 section).

The higher viscosity of the SOTD product indicates it is a larger molecule than the SSTD product. Therefore, during the thickening tests it would tend to form larger molecules when polymerizing with the lube oil. Thus, the polymerization characteristics of the SSTD product would be poorer than those of the SOTD product, i.e., higher viscosities would result.

### Milestone 3. Catalytic Decarboxylation

This section will be organized as follows: (1) the results of the catalytic decarboxylation tests will be presented (the effects of hydrogenation of both raw materials and products, a comparison of the alkali metal hydroxide decarboxylation of oil with the thermal decarboxylation of soap, and a comparison of the catalytic decarboxylation of soaps and oils), (2) the results of using catalysts other than alkali metal hydroxides, and (3) the results of further characterization studies determining the distillation and polymerization properties of decarboxylation products (results using a second vegetable oil and a second lubricating oil will also be included). Pertinent analytical data for the runs to be discussed are presented in Table 3.



Table 3. Catalytic Decarboxylation Results

Run No.	Form	Catalyst	Yields (wt%)		Max. Temp. (°F)	Distillate			
			Distillate	Water Bottoms		Viscosity (cSt)	Iodine Value	Acid Number	Density (g/ml)
5	Safflower Oil	Ca(OH) <sub>2</sub>	34.1	3.8	760	3.31	116	168	0.84
6	Safflower Oil	AlCl <sub>3</sub>	44.5	3.9	805	6.61	121	180	0.86
7	Safflower Oil	V-0601	51.3	2.3	800	3.89	95	186	0.85
8	Safflower Oil	None	68.5	1.5	825	4.50	101	170	0.85
11	Safflower Oil	Silica-magnesia	70.6	2.2	825	4.46	112	158	0.85
12**	Safflower Soap	Ca(OH) <sub>2</sub>	47.9	-	840	2.73	135	3	0.83
14	Safflower Oil	Zeolite "B"	72.2	3.5	825	6.54	111	140	0.85
15	Safflower Oil	HT-500	74.1	2.8	850	4.34	97	116	0.85
16	Safflower Oil	HT-400	73.9	2.4	850	4.21	101	137	0.85
17	Safflower Oil	UOP-S-6	78.0	2.4	840	4.69	96	127	0.85
18	Safflower Soap	HT-400	45.4	-	890	2.24	155	1	0.81
19	Safflower Soap	Zeolite "B"	24.2	-	850	2.50	160	3	0.83
22	Safflower Oil	UOP SPA-2	28.0	2.3	705	8.56	108	209	0.86
23	Safflower Oil	UOP-S-6	71.7	3.2	850	4.94	97	122	0.85
24**	Safflower Oil	None	73.4	1.1	850	6.76	97	163	0.87
25**	Safflower Soap	None	55.6	-	800	3.33	160	5	0.83
26	Safflower Soap	Ca(OH) <sub>2</sub>	45.3	-	900*	3.13	143	2	0.85
28**	Safflower Oil	HT-500	72.8	2.7	840	4.28	99	98	0.85
31	Safflower Soap	None	47.0	-	930*	2.97	147	1	0.83

\* Flask temperature

\*\* Denotes polymerization study was performed on this product



## Hydrogenation of Raw Materials and Products

The hydrogenated safflower oil was a hard, white solid at ambient conditions; the hydrogenated safflower oil that was converted to a calcium soap was also a hard, white solid at room temperature and pressure. Attempts to catalytically decarboxylate both these hydrogenated materials were unsuccessful because the condenser became plugged with solids and forced the experiments to be stopped. Five different decarboxylation experiments were made with hydrogenated materials (two catalytic decarboxylations and three thermal decarboxylations) without success. As previously mentioned in the discussion of Milestone 2, these products that clogged the condenser would be poor fuel substitutes because they are solid. Therefore, these products were not characterized and no polymerization studies were performed on them.

Products from the catalytic decarboxylation of safflower oil, rapeseed oil, and safflower soap were hydrogenated to evaluate the usefulness of a final saturation of the carbon bonds with hydrogen. Unfortunately, all the hydrogenated products were solids at ambient conditions, which would make them unacceptable as fuel substitutes -- no polymerization tests were performed on them. Similar results were obtained when thermal decarboxylation products of safflower oil and rapeseed soap were hydrogenated (Milestone 2).

## Catalytic Decarboxylation of Oils with Alkali Metal Hydroxides vs. Thermal Decarboxylation of Soaps

The literature survey had revealed that hydrocarbons could be synthesized by heating soaps of vegetable oils either with or without alkali metal hydroxides. This led to the hypothesis that heating a vegetable oil with an alkali metal hydroxide catalyst might result in a decarboxylation mechanism that would include a soap intermediate -- the products would then be similar to those from the thermal decarboxylation of soaps.

Duplicate catalytic decarboxylations with a calcium hydroxide catalyst (Runs 12 and 26) and thermal decarboxylations (Runs 25 and 31) were made with safflower soaps. From Table 3 data it is apparent that the distillate yields and product properties were similar for all four runs: yields ranged from 45.3 to 55.6 wt%, viscosities from 2.73 to 3.33 cSt, iodine values from 135 to 160, acid numbers from 1 to 5, and densities from 0.83 to 0.85 g/ml. Run 5 was the safflower oil that was catalytically decarboxylated with calcium hydroxide to compare with the soap products. The lower distillate yield compared to the soap products (34.1 wt% vs. 45.3-55.6 wt%) may have been due to not heating the product to a high enough temperature during the initial catalytic decarboxylation runs. Viscosities and densities were comparable for both oil and soap products; the iodine value of the oil product was slightly lower (116 vs. 135-160) and the acid number dramatically larger (168 vs. 1-5). The iodine values indicated that the oil



was slightly more saturated than the soaps and the acid numbers showed that the soaps had been decarboxylated much more extensively than the oil, i.e., there were more hydrocarbons and fewer fatty acids. The catalytic decarboxylation of the safflower oil was not duplicated because a number of other catalysts had already been tried prior to the thermal decarboxylations of the soaps. The products resulting from catalytic decarboxylation using mediocre catalysts such as calcium hydroxide were all similar. The oil and soap products were obviously not equivalent, and that indicated the reaction mechanisms were different for the two processes.

#### Catalytic Decarboxylation of Soaps vs. Oils

As discussed in the next section, decarboxylation catalysts other than calcium hydroxide were investigated. Three different catalysts (calcium hydroxide, Zeolite "B", and HT-400) were used to compare the use of safflower oil and safflower soap as feed materials. Pertinent Table 3 data includes the following experimental runs:

Catalyst	Safflower Oil	Safflower Soap
Calcium Hydroxide	Run 5	Runs 12,26
Zeolite "B"	Run 14	Run 19
HT-400	Run 16	Run 18

Distillate yields will be discussed relative to the Zeolite "B" and HT-400 catalysts only because the low yield using calcium hydroxide with safflower oil (Run 5) was probably due to not attaining a high enough decarboxylation temperature in the early experiments. For both catalysts the yields were significantly higher using the safflower oil rather than the safflower soap (72.2 and 73.9 wt% vs. 24.2 and 45.4 wt%).

Distillate properties varied consistently when comparing the use of oil and soap. The viscosities of the soap products were slightly lower (2.24-3.13 cSt) than those of the oil products (3.31-6.54 cSt). There was significantly more saturation in the oil products than the soap products (iodine values of 101-116 vs. 135-160); the higher saturation of the carbon-carbon double bonds in the oil products which should result in less polymerization with lube oil. The largest difference, however, was the notably lower acid numbers of the soap products relative to the oil products (1-3 vs. 137-168); low fatty acid content in the soap products should result in less polymerization with lube oil.

An interesting observation was that both the catalytic and thermal decarboxylation of the safflower soaps gave essentially the same products. This is obvious by comparing Table 3 data for the catalytic decarboxylations (Runs 12, 18, 19, and 26) with that for the thermal decarboxylations (Runs 25 and 31). The use of catalysts did not increase the product yields and, when the



Zeolite "B" catalyst was used (Run 19), the yield actually decreased. This indicates that safflower soaps should probably be thermally decarboxylated.

Although the polymerization tests will be discussed later in the Distillation and Polymerization Characteristics section the results will also be summarized here. The distillate from the catalytic decarboxylation of the safflower oil had a rapid increase in kinematic viscosity after about 30 hours, but then leveled off after about 50 hours. However, a thick sludge formed that settled to the bottom of the vessel used to measure thickening properties; this sludge would undoubtedly prove detrimental to engine operation should this product be used as a diesel fuel. The catalytic decarboxylation of the safflower soap gave a distillate that had a very slow increase in kinematic viscosity with time -- this product appears to be promising for use as a diesel fuel.

#### Catalyst Studies

Based on the literature search prepared as part of Milestone 1, it was obvious that catalysts other than alkali metal hydroxides had shown promise for the decarboxylation of vegetable oils. Aluminum chloride, oxides of phosphorous and vanadium, silica-alumina, and silica-magnesia were among these other catalysts that were tested. In addition, a number of hydrocracking catalysts that contained various mixtures of molybdenum, nickel, and cobalt were investigated.

Table 3 data shows that the highest product yields from safflower oil (71.7-78.0 wt%) were obtained using hydrocracking catalysts -- Harshaw HT-500 (Ni-Mo, Runs 15 and 28), Harshaw HT-400 (Co-Mo, Run 16), and Universal Oil Products UOP-S-6 (Co-Ni-Mo, Runs 17 and 23). The kinematic viscosities of the products (4.21-4.94 cSt) were similar to those of No. 2 diesel fuel and substantially lower than the raw oil viscosity of 28.6 cSt. Silica-magnesia catalyst (Run 11) also produced a similar product. Poor catalysts were the aluminum chloride (Run 6) and the phosphorous oxide (UOP SPA-2, Run 22) which resulted in low product yields and kinematic viscosities greater than 6 cSt. The silica-alumina (Zeolite "B", Run 14) gave a high product yield but an unacceptable product viscosity while vanadium oxide (Run 7) gave a low product yield but an acceptable product viscosity.

#### Distillation and Polymerization Characteristics

A decision on which products to subject to further characterization studies was based on distillate yields and properties. Even though the UOP-S-6 catalyst had resulted in slightly higher yields, the safflower oil products resulting from the use of the Harshaw HT-500 catalyst were selected because: (1) they had the lowest acid number, (2) they had a lower viscosity than the UOP-S-6 products, and (3) more was known about the composition of the



HT-500 catalyst than the UOP-S-6 catalyst. For safflower soap products, the products resulting from the use of the calcium hydroxide catalyst were selected for further characterization studies.

Product characterization data for products from the thermal decarboxylation of safflower oil and soap that was included in the Milestone 2 discussion will also be discussed in this section to provide a comparison of catalytic and thermal decarboxylation.

The duplicate runs whose Table 3 data had been used to make the above decisions were: catalytic decarboxylation of safflower oil (SOCD - Runs 15 and 28), catalytic decarboxylation of safflower soap (SSCD - Runs 12 and 26), thermal decarboxylation of safflower oil (SOTD - Runs 8 and 24), and thermal decarboxylation of safflower soap (SSTD - Runs 25 and 31). For each type of decarboxylation study, the product from one of the duplicates was used to obtain distillation data while the product from the other duplicate was used for the polymerization test.

Table 4 distillation data shows that, although the safflower oil products had a lower initial boiling point than the safflower soap products, the soap products generally had the lower boiling point components (this was true for both catalytic and thermal decarboxylation products). Therefore, the soap products would be more volatile fuels than the oil products.

In Figure 2, the polymerization results are shown as a plot of kinematic viscosity of a 5 wt% solution of the product distillate in the Phillips SAE 30W lube oil as a function of time. For the oil products a rapid increase in kinematic viscosity was noted after 20 hours for the thermal decarboxylation products and after 30 hours for the catalytic decarboxylation products. In addition a substantial quantity of very thick, semi-solid material was formed with both SOTD and SOCD products. This sludge was much thicker than the remaining oil and tended to settle to the bottom of the vessel. As the sludge was formed it most likely caused the tapering-off of the rapid viscosity increase noted above. The decarboxylation products forming the sludge were not available for thickening the remaining lube oil and were probably not collected in the viscosity samples; thus, the curves in Figure 2 do not represent a true picture of viscosity change with respect to time. The surfaces of the copper strip used in the polymerization tests were also covered with a layer of hard, black material for both the SOTD and SOCD products. This sludge would also undoubtedly clog filters, should these products be used as diesel fuel.

However, Figure 2 indicates that the soap products had a slow rise in kinematic viscosity with respect to time -- the curves are almost identical for both the catalytic and thermal decarboxylation products. No sludge was formed, and the surfaces of the copper strip were clean for both soap product tests. The soap products appear to be very promising for use as a diesel fuel.

Table 4. Distillation Characteristics of Decarboxylation Products

Run No.	Product	Total Dist. (vol%)	Temperature (°F) at Volume Distilled										
			Initial	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%
15	SOCD*	70	131	206	260	390	458	507	562	588	605	-	-
24	SOTD	60	145	165	345	430	453	560	587	620	-	-	-
26	SSCD	70	175	260	292	340	402	472	548	604	620	-	-
31	SSTD	76	176	263	295	365	423	470	525	588	635	-	-

\* SOCD - catalytically decarboxylated safflower oil  
 SOTD - thermally decarboxylated safflower oil  
 SSCD - catalytically decarboxylated safflower soap  
 SSTD - thermally decarboxylated safflower soap



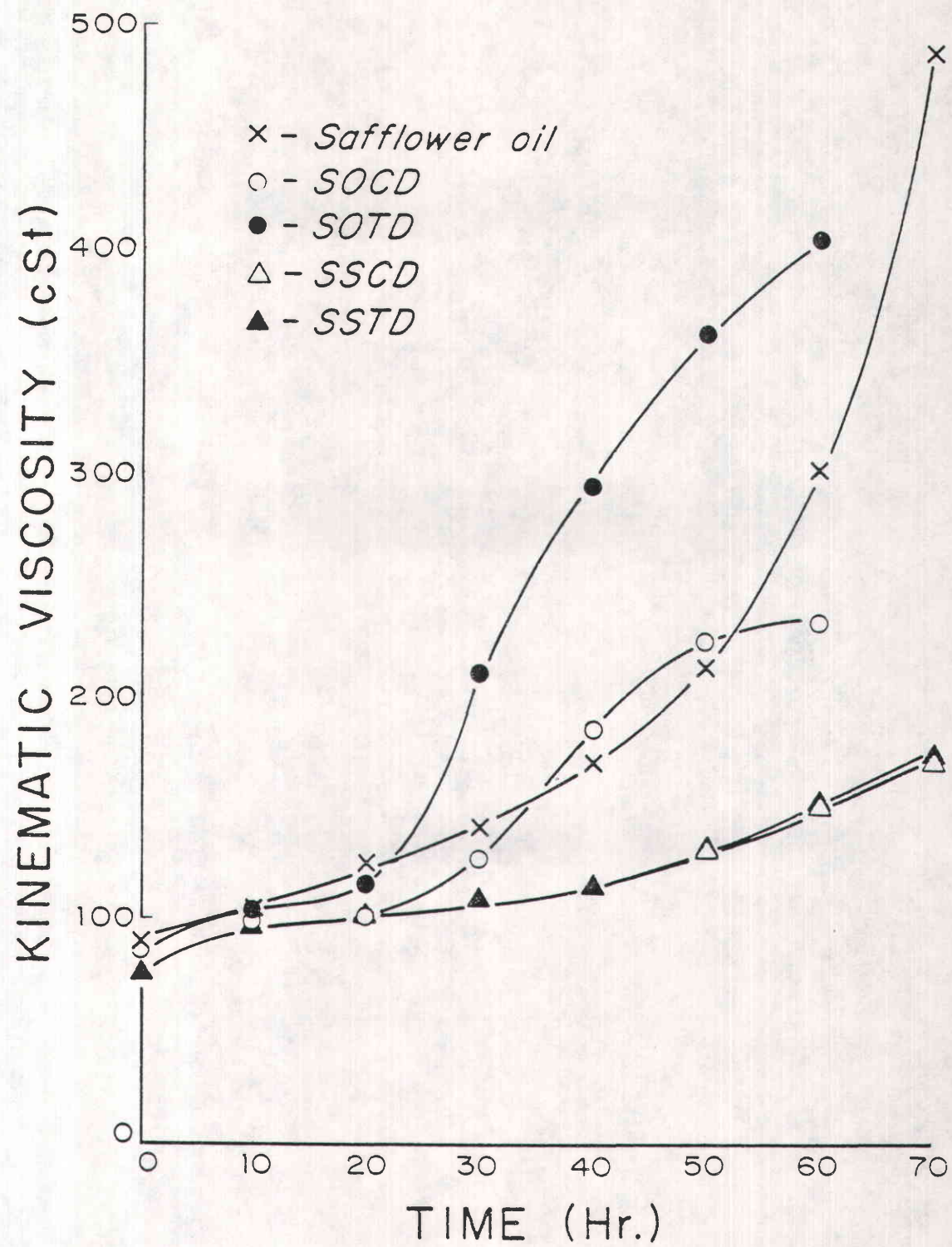


Figure 2. Polymerization Characteristics of Thermal and Catalytic Decarboxylation Products of Safflower Oil and Safflower Soap in Automotive Lube Oil

Even though the iodine values of the soap products were much higher than those of the oil products (135 and 160 compared to 99 and 97), they did not polymerize nearly as much. This shows that unsaturation of the carbon-carbon bonds is not the only contributor to the polymerization of lube oils. The acid numbers of the oil products were much higher than those of the soap products (98 and 163 compared to 3 and 5); this indicates the oils had a significantly higher free fatty acid content. As mentioned in the Milestone 2 section, it is possible that the carboxyl component of the fatty acid could promote polymerization of the lube oil. This theory is supported by the fact that raw safflower oil is easily decomposed into its constituent fatty acids and glycerol and polymerizes lube oil extensively.

The  $^{13}\text{C}$  NMR analyses verify the information obtained from the iodine values and acid numbers. Both unsaturation and chemical functional groups were identified using  $^{13}\text{C}$  NMR. Measurements were made on neat safflower oil as well as on products from the catalytic decarboxylation of the oil, from hydrotreating of the oil, and from the thermal decarboxylation of the soap. The safflower oil was much more unsaturated than the products from any of the three processes -- the saturation appeared comparable for all the products. However, there was a variety of functional groups combining carbon and oxygen. Oxygen was present as ester groups in the safflower oil, as carboxyl (acid) groups in the catalytic decarboxylation and hydrotreating products, and as carbonyl (ketone) groups in the soap thermal decarboxylation product. It is probable that the carboxyl groups in the products or that are formed by the decomposition of the esters contribute significantly to polymerization with the lube oils. The carbonyl groups resulting from the thermal decarboxylation of the soaps apparently do not promote polymerization. Previous research discovered during the literature search also supports these interpretations. Several instances were found where the heating of vegetable oils resulted in polymerization into dibasic acids, i.e., compounds containing two carboxyl (acid) groups. This indicates that neat vegetable oils will likely have carboxyl groups present just as the products from catalytic decarboxylation and from hydrotreating do. Earlier researchers had also detected the presence of ketones when soaps were thermally decarboxylated which confirms the present findings. There were some references indicating that the catalytic decarboxylation of calcium soaps using calcium hydroxide might form hydrocarbons rather than ketones. Unfortunately, no  $^{13}\text{C}$  NMR measurements were made on these products (Runs 12 and 26) to determine if both carboxyl (acid) and carbonyl (ketone) groups were absent.

Another factor to be considered is that the oil products had slightly higher viscosities than the soap products (4.28 and 6.76 cSt compared to 2.73 and 3.33 cSt). Heavier components would increase the thickening rate by forming larger molecules upon polymerizing.



Rapeseed oil was the second vegetable oil selected for decarboxylation studies. Unfortunately, the rapeseed oil and rapeseed soap tests had been completed before commercial analysis verified that we had been supplied with contaminated rapeseed oil. However, the polymerization data will be included to verify that automotive and railroad lubricating oils have significantly different polymerization properties after the addition of vegetable oil fuels. The polymerization results for products of the contaminated rapeseed oil might indicate trends that would be followed by rapeseed oil products, but this is uncertain because of the presence of the unknown solvent.

The results of the further product characterization studies on safflower oil and soap were used to select the rapeseed oil and soap products. The Harshaw HT-500 catalyst was used for the catalytic decarboxylation of the rapeseed oil (products were denoted as ROCD). No thermal decarboxylation of rapeseed oil was pursued because thermal decarboxylation had been shown to be inferior to catalytic decarboxylation when used with safflower oil. No apparent differences had been noted between the products of safflower soap catalytic and thermal decarboxylation; therefore, only the thermal decarboxylation of rapeseed soap was studied (RSTD was used to identify these products). Duplicate catalytic and thermal decarboxylation runs were made using the "rapeseed" oil.

Figure 3 presents the results of the polymerization tests as a plot of kinematic viscosity with respect to time. The same trends were noted with the rapeseed products as with the safflower products: (1) the kinematic viscosity of the rapeseed oil product increased rapidly after about 30 hours and a black sludge formed which coated the surfaces of the copper strip, and (2) the kinematic viscosity of the soap product rose very slowly with respect to time. The viscosities of the rapeseed products were consistently lower than those of the safflower products but this was probably because of the contaminating solvent present in the rapeseed products. However, the positive result of the rapeseed tests was that it can be expected that both safflower and rapeseed oil would produce similar substitute diesel fuels.

The railroad lube oil obtained from Burlington Northern was also used to investigate the polymerization properties of the decarboxylation products. The rapeseed products had appeared superior to the safflower products before it had been determined the former were contaminated; therefore, both the catalytic decarboxylation product of the rapeseed oil and the thermal decarboxylation product of the rapeseed soap were tested. After the rapeseed oil contamination problem had been identified, another thermal decarboxylation run was made with safflower soap to provide products for a polymerization study with the railroad lube oil. The railroad lube oil test results are presented in Figure 4. Unlike the automotive lube oil, all tests resulted in unacceptably high viscosities as time progressed. In fact, the polymerization test using the safflower soap products could not be finished



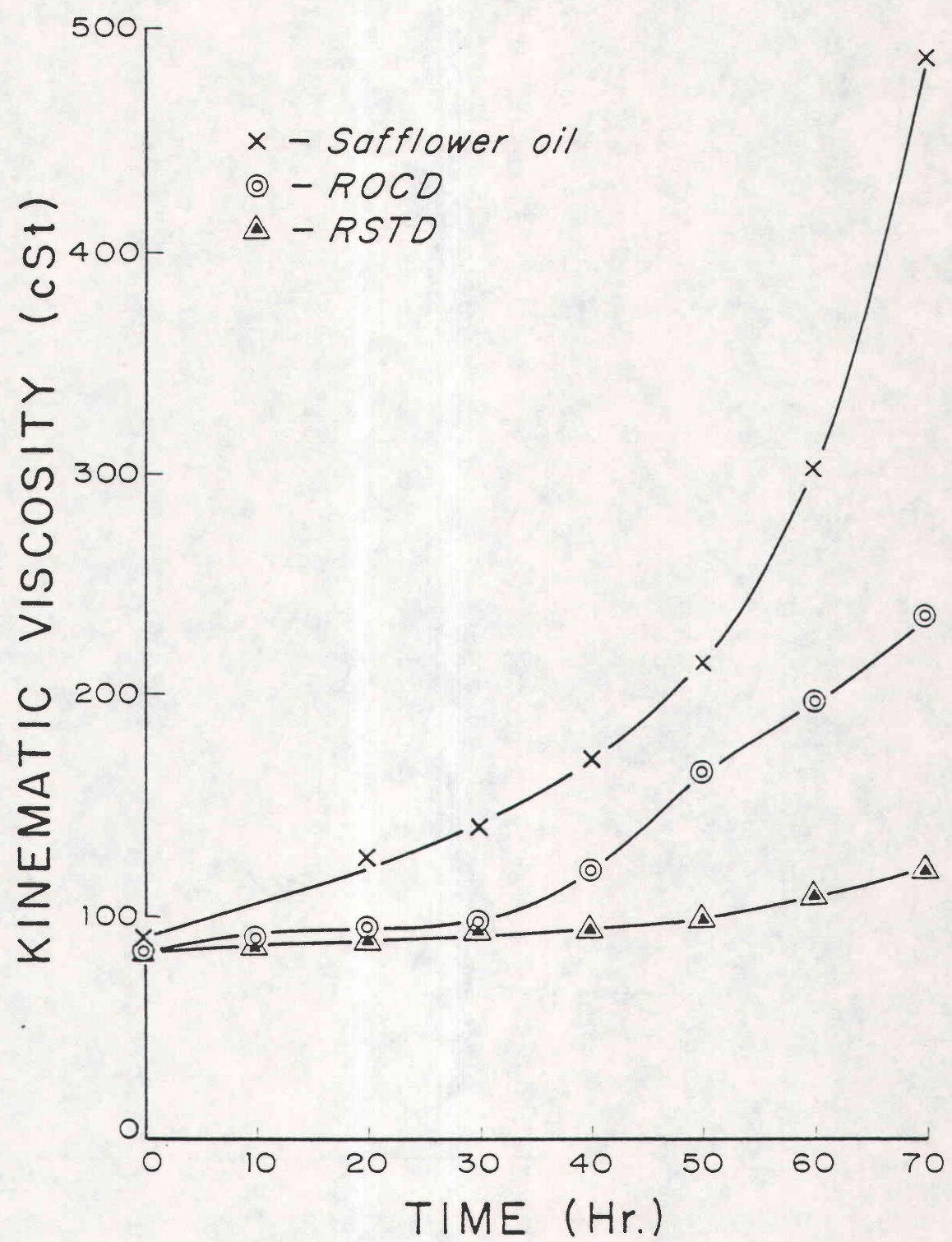


Figure 3. Polymerization Characteristics of Thermal and Catalytic Decarboxylation Products of "Rapeseed" Oil and "Rapeseed" Soap in Automotive Lube Oil



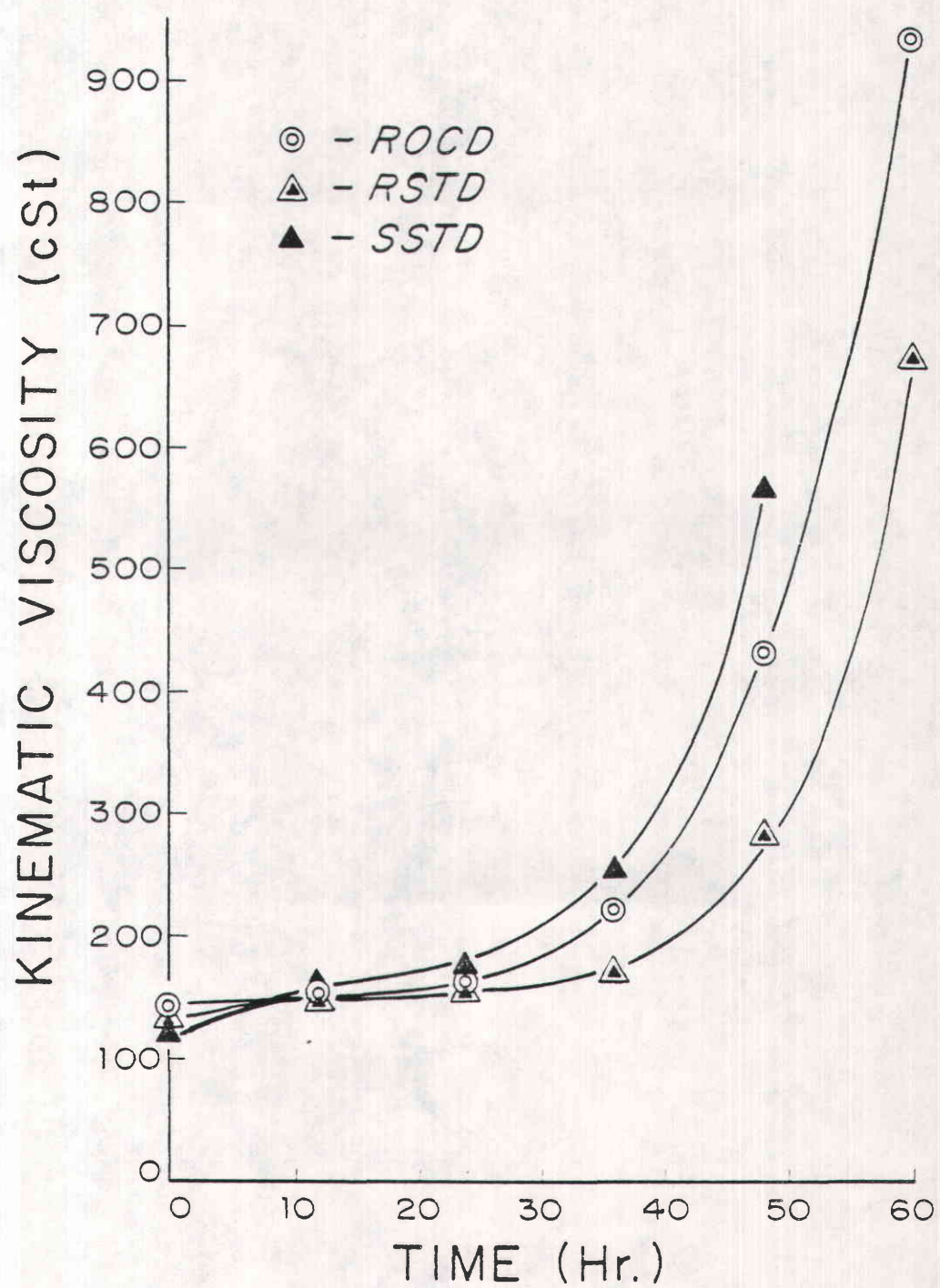


Figure 4. Polymerization Characteristics of Thermal Decarboxylation Products of Safflower and "Rapeseed" Soaps and of "Rapeseed" Oil in Railroad Lube Oil



because so much sludge had formed that the entire contents of the vessel turned black, and viscosities rose beyond the capabilities of the measuring apparatus. However, no sludge was formed with either rapeseed decarboxylation product and automotive oil. The poorer polymerization results with the railroad lube oil relative to those with the automotive lube oil were probably due to the additives in each lube oil -- different compounds are added to all lubricating oils to control their properties depending on the service for which they have been designed. It appears that vegetable oil decarboxylation products do not appear to be promising for use with standard railroad lube oils.

#### Milestone 4. Hydrotreating

Hydrotreating combines hydrogenation with catalytic and thermal decomposition. Theoretically, by combining these steps, high molecular weight compounds can be cracked into lower boiling materials. The severity of the process is increased by operating at higher temperatures and pressures, i.e., large molecules are decomposed into smaller molecules. Hydrotreating is an important process used in the petroleum industry for breaking heavy crude oil feedstocks into usable gasoline and diesel range products; however, a literature search indicated that very little research has been done to determine the effects of hydrotreating on vegetable oils.

The purpose of this milestone project was to conduct a preliminary investigation of hydrotreating effects on vegetable oils, and compare the products with those obtained from thermal and catalytic decarboxylation of safflower oil and safflower soap. The effects of temperature, pressure, and catalyst type on product properties (especially viscosity) were the major areas of interest along with evaluating the tendency of the best resulting product to polymerize with typical diesel engine lubricating oil.

#### Hydrotreating

Three temperature levels (350, 400, 450 C), two pressure levels (500 and 1,000 psig), and two catalysts (NiT and NiMo) were investigated. The normal hydrotreating temperature range for petroleum processing is 300-500 C. As the temperature increases the cracking mechanism changes from a carbonium ion mechanism to a free radical mechanism with an increase in yields of low-molecular-weight products unsuitable for diesel fuel. Therefore, it was decided to investigate the lower temperature range. Increases in yields of diesel fuel seem to be obtained at lower pressures for petroleum feedstocks. The pressure must be high enough to promote the hydrogenation process, but low enough to hinder the formation of low-molecular-weight range products. Thus a moderate pressure range was selected for the experiments. Two fairly common hydrotreating catalysts were on hand - a Harshaw nickel-molybdate catalyst (HT-500 E 1/16") composed of 16 wt% molybdenum trioxide and 16 wt% nickel oxide on an alumina base and



a Harshaw nickel-tungsten catalyst (Ni-4303 E 1/12") composed of 19 wt% tungsten and 6 wt% nickel on an alumina base.

A factorial experimental design was used to evaluate the effects of the process variables. In this type of design an experiment is run at every combination of the process variables at each of their possible levels. Thus, twelve experiments were required for this study (Table 5). Another characteristic of experimental designs is that the order in which the experiments are performed is selected randomly - this avoids introducing a bias that might be generated due to changes in experimental techniques or feedstocks.

Two criteria, viscosity and acid number, were used to determine which experimental run should be repeated to give enough product for the distillation characterization and polymerization study. As previously discussed, a qualitative measure of viscosity was used to determine the superior runs that gave the lowest viscosity product. Originally it had been anticipated that iodine values would be helpful to identify promising products because they provide a measure of saturation. It was believed that the higher saturation led to less polymerization. However, during thermal decarboxylation experiments (Milestone 2 tests), it appeared that the acid number was a better indicator of polymerization tendencies. Lower acid numbers indicate lower fatty acid contents and usually less tendency to polymerize. Because not enough product was available for measuring both the acid number and the iodine value, only the acid number was measured.

The effects of temperature on the product viscosities for the nickel-tungsten (NiT) catalyst runs indicated that initially hydrogenation dominated giving way to cracking at the higher temperatures. This was evident by the increase in viscosity at mid-temperatures as a result of saturation with little cracking followed by a pronounced decrease in viscosity at higher temperatures (Figure 5). This viscosity decrease was probably caused by the larger saturated molecules being broken down into shorter molecules. The oil at 350 C looked much like the raw oil; this was surprising, because it had been reported that decomposition or discoloration would take place near 200 C.

Temperature effects with the nickel-molybdate (NiMo) catalyst were dependent on pressure except at the high temperature, 450 C (Figure 5). At the low pressure, the temperature effects on viscosity in the NiMo runs were similar to those in the NiT runs, i.e., an initial viscosity increase was followed by a decrease as the temperature was increased. At the high pressure the viscosity decreased with increasing temperature. Similar to the NiT catalyst, the highest temperature (450 C) resulted in the lowest viscosity products. At the low temperature (350 C), the products using the NiMo catalyst were much more viscous than those using the NiT catalyst, and discoloration of the former products was evident.



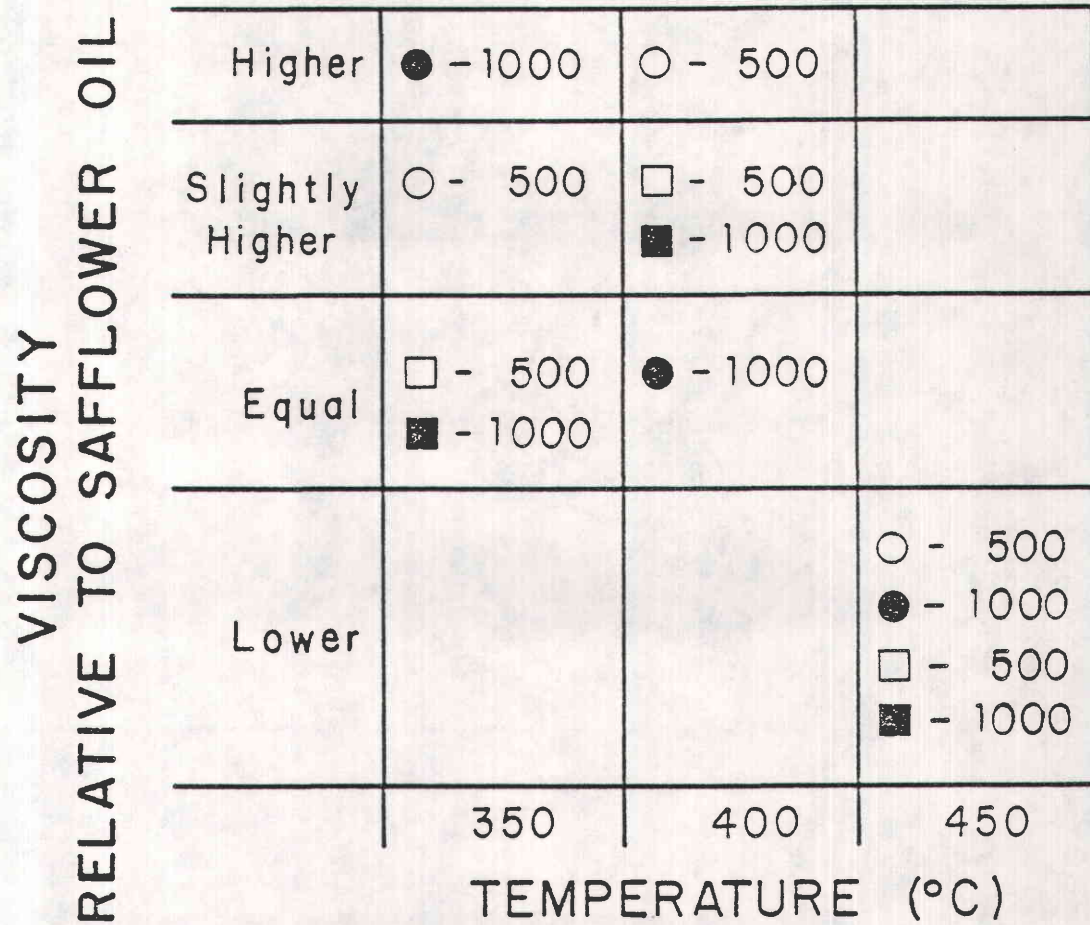
Table 5. Effects of Hydrotreating Process Variables on Product Characteristics

Run No.	Temperature (C)	Pressure (psig)	Catalyst	Relative Viscosity*	Acid Number
1	350	500	NiT	2	-
2	400	500	NiT	3	-
3	450	1000	NiMo	1	107
4	450	500	NiT	1	42
5	400	1000	NiT	3	-
7	350	1000	NiT	2	-
8	350	1000	NiMo	4	-
9	400	1000	NiMo	2	-
10	400	500	NiMo	4	-
11	450	1000	NiT	1	80
12	350	500	NiMo	3	-
13	450	500	NiMo	1	88

\* Compared to raw safflower oil:

- 1 - lower
- 2 - equal
- 3 - slightly higher
- 4 - higher





Catalysts | Pressure (psig)

NiMo ○ 500

NiMo ● 1000

NiT □ 500

NiT ■ 1000

Figure 5. Relative Viscosity vs. Temperature for Hydrotreated Safflower Oil



Pressure seemed to have no effect on the viscosity of NiT products (Figure 6). As mentioned above, there seemed to be a pressure-temperature interaction effect on the viscosities of the products using the NiMo catalyst: at 350 C the viscosity increased as the pressure was increased, at 400 C the viscosity decreased as the pressure was increased, and there was no apparent effect of pressure on viscosity at 450 C.

It is evident that the NiT catalyst products generally had lower viscosities than those generated using the NiMo catalyst. However, at 450 C both catalysts produced low viscosity products at both pressure levels.

Four experimental runs (HT-3, HT-4, HT-11, HT-13) resulted in products having viscosities lower than the starting safflower oil; therefore, the acid number was used to select the run that should be replicated to produce enough product for further testing. As seen in Table 5, product from run HT-4 had a significantly lower acid number (42) than products from the other three runs; therefore, the most promising variable levels indicated by this investigation were 450 C, 500 psig, and a NiT catalyst.

Five runs were made at run HT-4 conditions, and each was carried out using a much larger amount of oil than for the factorial experimental design tests. As previously mentioned, the hydrogen to oil ratio was significantly decreased because the volume of the reactor remained constant. This decreased ratio may have been responsible for the increase in fatty acids in the products - the acid numbers for the five tests ranged from 71 to 87 compared to an acid number of 42 for the previous test using a higher ratio of hydrogen to oil.

The products from the five additional runs were combined for further testing, and will be referred to as the hydrotreating product. Distillation of the hydrotreating product showed very little decomposition. The initial boiling point (117 F) was well below any oil or soap thermal decarboxylation products (Milestone 2). The initial distillate (first 5 vol%) was a very clear liquid but, as the distillation continued, the distillate became a milky yellow color. After cooling, the liquid darkened to a deep brownish-black color (probably from oxidation). The distillate contained less than 0.5 vol% water while the residue was a very viscous, tar-like substance. About 78 vol% of the hydrotreating product was found to be in the grade 2-D diesel fuel range (distilling under 640 F). Nearly 60 vol% was in the grade 1-D diesel fuel range (distilling under 550 F). The hydrotreating distillate is compared to those distillates of the thermal decarboxylation products (Milestone 2) in Table 6. The kinematic viscosity of the distillate was 1.85 cSt compared to 4.91 cSt for the total hydrotreating product. This compares to kinematic viscosities of 1.3-2.4 cSt for grade I-D diesel fuel and 1.9-4.1 for grade 2-D.



VISCOSITY  
RELATIVE TO SAFFLOWER OIL

Higher	● - 400	○ - 350
Slightly Higher	○ - 350 ■ - 400	■ - 400
Equal	□ - 350	● - 400 □ - 350
Lower	● - 450 ■ - 450	● - 450 ■ - 450
	500	1000
PRESSURE (psig)		

*Catalysts* | *Temperature (°C)*

NiMo ● 450  
 NiMo ○ 400  
 NiMo ○ 350  
 NiT ■ 450  
 NiT ■ 400  
 NiT □ 350

Figure 6. Relative Viscosity vs. Pressure for  
Hydrotreated Safflower Oil



Table 6. Distillation Characteristics of Products

Product*	Total Dist. (vol%)	Temperature (°F) at Volume Distilled										
		Init.	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%
SOHT	78	117	180	245	330	400	450	515	555	575	-	-
SOTD	60	145	165	345	430	453	560	587	620	-	-	-
SSTD	76	176	263	295	365	423	470	525	588	635	-	-

\* SOHT - hydrotreated safflower oil

SOTD - thermally decarboxylated safflower oil

SSTD - thermally decarboxylated safflower soap



## Polymerization

The distillate from the hydrotreating product was used for the polymerization test. The results of the test are summarized in Figure 7 where they are compared to the raw safflower oil and thermal decarboxylation products from Milestone 2.

During the first ten hours the viscosity increased over 20 percent. For the next twenty hours almost no thickening occurred. At thirty hours the viscosity increased as a fairly rapid, constant rate until leveling out after about sixty-five hours. This same "S-shaped" curve was obtained using the product obtained from the thermal decarboxylation of safflower oil. Again, this curve shape is probably because of the formation of a "sludge". The sludge from the hydrotreating product was much lighter than the heavy sludge from the thermally decarboxylated safflower oil; it was not a semi-solid material and would go into solution quite easily by stirring the lube oil. The nature of this sludge suggests there is a good chance that the hydrotreating processing variables could probably be adjusted to produce a product that would not polymerize in the engine crankcase.

This preliminary investigation was intended to evaluate the potential of the hydrotreating process for converting vegetable oils to diesel fuel rather than to provide exhaustive information about the process. Table 7 provides a comparison of hydrotreating product with those from the Milestone 2 thermal decarboxylation investigation. The yield of diesel fuel using hydrotreating is higher than for any other process. Hydrotreating also gives the product with the lowest viscosity, and is one of the more saturated products as indicated by the fairly low iodine value. The fatty acid content is much lower than products obtained from the oils but much higher than those obtained from the soaps. The  $^{13}\text{C}$  NMR measurements showed that the presence of carboxyl (acid) groups probably caused the polymerization when added to the automotive lube oil (see the discussion of  $^{13}\text{C}$  NMR results in the Milestone 3 section). While it has been shown that the soap products do not have polymerization problems, they have the disadvantage of requiring an additional process to convert the oils to the soaps. Hydrotreating, on the other hand, is a relatively straightforward, simple process which would convert the vegetable oil into a liquid that could be distilled to recover the diesel fuel product.

Based on the above information it appears that a more thorough investigation of hydrotreating vegetable oils to produce diesel fuel is justified.

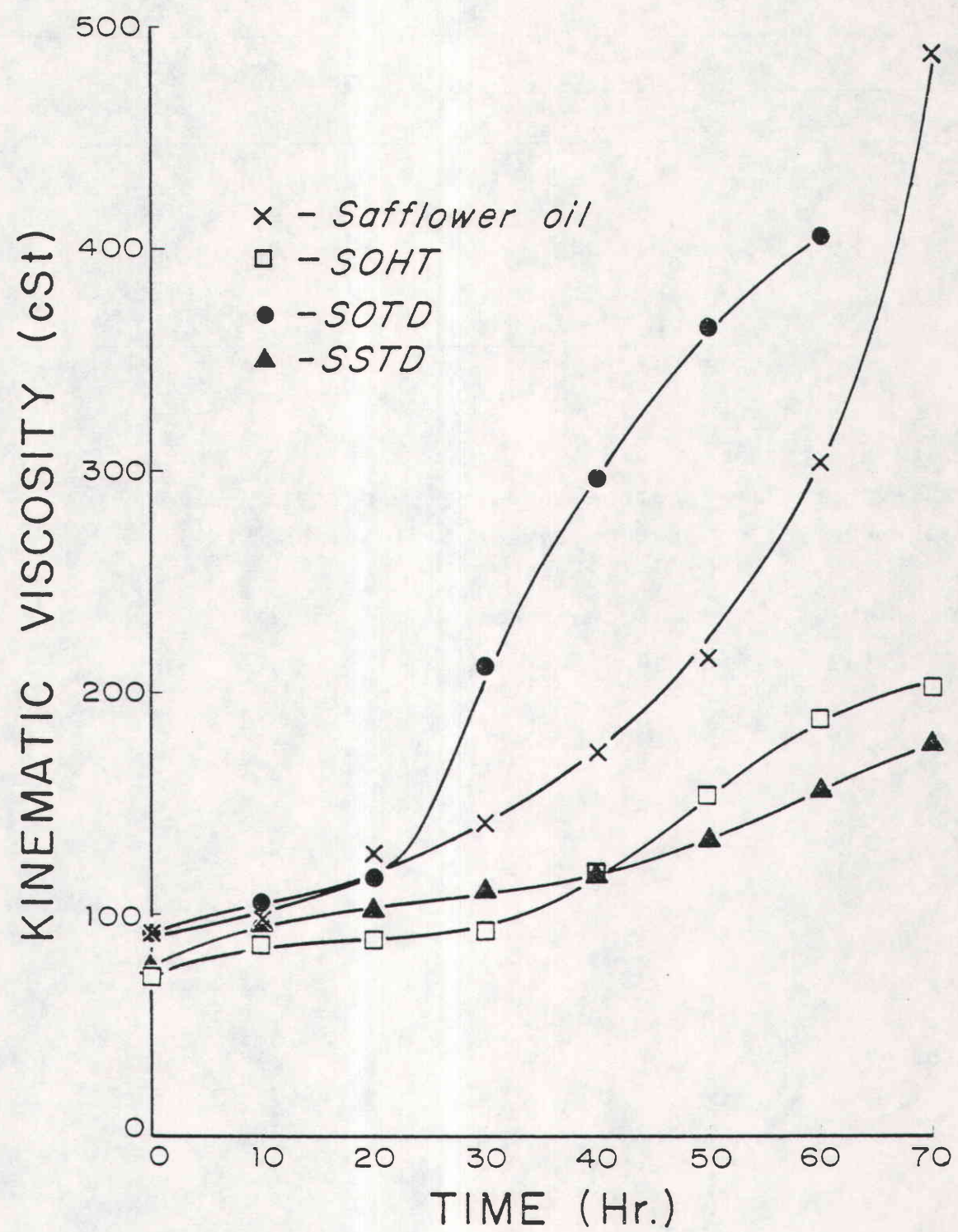


Figure 7. Polymerization Characteristics of Various Safflower Oil and Safflower Soap Fuels



Table 7. Product Characteristics

Product	Yields		Viscosity (cSt)	Iodine Value	Acid Number
	Total Liquid (wt %)	Distillate (vol %)			
SOHT*	84	78	1.85	60	81
SOTD	73	60	6.76	97	163
SSTD	56**	76	3.33	160	5

\* SHOT - hydrotreated safflower oil

SOTD - thermally decarboxylated safflower oil

SSTD - thermally decarboxylated safflower soap

\*\* This yield does not account for any losses that may occur while converting the oils to soaps.

## CONCLUSIONS AND RECOMMENDATIONS

The most important result of this project has been the production of a vegetable oil fuel that does not result in significant polymerization when mixed with automotive lubricating oil - the fuel is produced by both the thermal decarboxylation and catalytic decarboxylation of safflower oil soap. Further, in the decarboxylation products of the vegetable oil soap, carbon and oxygen are present as carbonyl (ketone) functional groups; this probably accounts for their favorable polymerization characteristics. Unfavorable fuels (those that polymerized with lube oil) were produced by both the thermal decarboxylation and catalytic decarboxylation of safflower oil and by the hydrotreating of safflower oil. However, the hydrotreated oil showed less polymerization than the thermally and catalytically decarboxylated oil. The carbon-oxygen functional groups present in these unfavorable fuels were either carboxyl (acid) or ester groups (ester groups are easily converted to carboxyl groups). It also appears that, relative to the chemical structure of the vegetable oil fuels, the presence of carboxyl groups is more significant than the existence of unsaturation (double bonds between adjacent carbon atoms) when it comes to promoting polymerization. Hydrogenation was shown to be useless in this application because it results in solid fuels at ambient conditions making it unsuitable for use as a diesel fuel. This occurred with the vegetable oil itself as well as with products from oil that was hydrogenated before and after decarboxylation. An attempt to evaluate the polymerization properties of rapeseed oil products was unsuccessful because the sample of rapeseed oil being used for processing was contaminated. The fuels that did not polymerize when mixed with automotive lube oil did polymerize when mixed with railroad lube oil. This is probably a result of differences in the lubricating oil additives (additives are adjusted according to the service for which the lubricants are intended).

This project has successfully identified a vegetable oil fuel practically free from polymerization properties. As an exploratory study, however, its purpose was to discover a type of vegetable oil fuel suitable for use as a diesel fuel rather than to thoroughly investigate the process for its production. A process study should now be initiated to investigate the following areas for improving the efficiency and effectiveness of the process:

1. Thermal Decarboxylation Studies. All properties of the soap should be identified that will affect the yield and polymerization properties of the fuel.
2. Catalytic Decarboxylation of Soap for Use with Medium-speed Diesel Engines. It may be possible through the use of a particular catalyst, an alkali hydroxide, to completely remove oxygen from the soap products -- this might result in a fuel that would not polymerize with railroad lubricating oil and open up a significant new market for safflower fuel.



3. Soap Production. A simpler soap production process should be developed. These experiments were based on commercial processes that include many steps to improve the cosmetic properties of the soap. It is likely that these can be modified or eliminated when the ultimate product is fuel.

4. Fatty Acid Unsaturation Studies. Although unsaturation may be less important in promoting polymerization than previously thought, polymerization from this cause should be measured.

Process Optimization. After the thermal decarboxylation and soap production process variables have been identified, an optimization technique should be used to adjust them until the best possible fuel yields and polymerization properties are found.

6. Hydrotreating. This process produces products with low viscosity and unsaturation. Although hydrotreating product did polymerize when mixed with lube oil, it was considerably better than the oil and decarboxylated oil products. Polymerization problems might be eliminated through a more thorough process investigation.

# TABLE OF ABBREVIATIONS

Al - aluminum  
 $\text{AlCl}_3$  - aluminum chloride  
 AN - acid number  
 ASTM - American Society for Testing and Materials  
 C - degree centigrade  
 $\text{Ca(OH)}_2$  - calcium hydroxide  
 Co - cobalt  
 cSt - centistoke  
 F - degree Fahrenheit  
 g - gram  
 gal - gallon  
 IV - iodine value  
 KOH - potassium hydroxide  
 ml - milliliter  
 mm Hg - millimeters of mercury  
 Mo - molybdenum  
 NaOH - sodium hydroxide  
 Ni - nickel  
 psi - pounds per square inch  
 psig - pounds per square inch gauge  
 ROCD - rapeseed oil, catalytic decarboxylation  
 RSTD - rapeseed soap, thermal decarboxylation  
 SAE - Society of Automotive Engineers  
 SAE 30W - SAE lubricating oil viscosity classification 30W  
 SAE 45 - SAE lubricating oil viscosity classification 45  
 SCF - standard cubic feed  
 sec - second  
 SOCD - safflower oil, catalytic decarboxylation  
 SOTD - safflower oil, thermal decarboxylation  
 SSCD - safflower soap, catalytic decarboxylation  
 SSTD - safflower soap, thermal decarboxylation  
 V - vanadium



APPENDIX

LITERATURE SURVEY ADDRESSING THE CONVERSION  
OF VEGETABLE OILS INTO ENGINE FUELS

LITERATURE SURVEY ADDRESSING THE  
CONVERSION OF VEGETABLE OILS INTO ENGINE FUELS

INTRODUCTION

Two principal problems have been identified with using vegetable oils directly as diesel fuels: (1) vegetable oils form carbon deposits inside direct injection engines and (2) vegetable oils carried into the crankcase polymerize with the lubricating oil leading to eventual engine failure. Both problems are related to the differences in chemical structure between vegetable oils and diesel fuels.

Vegetable oils are esters formed by the combination of glycerol with three fatty acids. These fatty acids are straight-chained, monocarboxylic acids that can be either saturated or unsaturated. Carbon deposits can be avoided by either using indirect injection engines or by transesterification. The net effect of transesterification is to replace one large triglyceride molecule with three smaller esters. The principal change in physical characteristics of the transesterified vegetable oils is a significant reduction in viscosity compared to unmodified vegetable oils. This lowering of the viscosity appears to prevent the formation of carbon deposits.

Transesterification, however, does not reduce the polymerization problem. Polymerization is caused by either the carbon double bonds (present in all crude vegetable oils) or the carboxyl groups. As the oils polymerize, either the lubricating properties of engine oil are destroyed or gums are formed which plug filters and lines.

Polymerization problems may be solved by modifying the chemical structure of the vegetable oils to eliminate unsaturated carbon bonds and/or the carboxyl groups. The double bonds can be removed by hydrogenation but this results in a fuel that is a solid at room temperature. The removal of the carboxyl group (decarboxylation) could most easily be accomplished by thermal or catalytic cracking. Decarboxylation with subsequent hydrogenation would result in a liquid hydrocarbon product that has essentially the same chemical structure as diesel fuels.

The conversion of vegetable oils to engine fuels is not a new concept, and it was decided to search the literature for pertinent process research that resulted in the formation of hydrocarbon fuels. There were two periods of research in this field: (1) the early period during the first half of this century and (2) the current period. Both periods will be reviewed in turn, and then integrated into a discussion of potential conversion processes. Although both decarboxylation and hydrogenation are important to the production of diesel fuels, it was found that very little information was available concerning the effects of hydrogenation. Therefore, the review primarily addresses decarboxylation with only



a few references related to hydrogenation. However, past research relevant to both decarboxylation and hydrogenation are interpreted in a summarizing section.

#### CHRONOLOGICAL SURVEY OF RESEARCH

##### Early Period

Following is a chronological summary of major decarboxylation experiments performed between 1888 and 1951. Data from these early experiments will be presented even though its accuracy is questionable. Yields are difficult to compare since many different methods were used to calculate product yields.

The thermal or catalytic decarboxylation of vegetable oils has been studied for nearly 100 years starting with the work of Engler in Germany. In 1888 he synthesized hydrocarbons from vegetable oils in order to support the theory that petroleum originated from organic materials.[1]

Pictet and Potak reported in 1919 that the low pressure (13-15 mm Hg), dry distillation of sodium stearate produced a mixture of saturated hydrocarbons. These hydrocarbons ranged from C10 to C34. [2,3]

In 1920 Grun and Wirth also pyrolyzed sodium stearate at 550-600 C and atmospheric pressure to produce about a 60 percent yield of mostly unsaturated hydrocarbons. [4]

The French scientist, A. Mailhe, did extensive work on decarboxylation of oils in the early 1920's. He was the first to decompose oils using catalysts. Both plant and animal oils were heated to 400-450 C in the presence of various catalysts in liquid-phase and vapor-phase experiments. Liquid products similar to gasoline were obtained that contained linear, cyclic, and aromatic hydrocarbons. Mailhe also observed the presence of free fatty acids in all products. From his observation that similar products were obtained from oils of various origins, Mailhe postulated that carboxylic acids were the precursors of the hydrocarbons. [5-13]

Most of the studies done by these European scientists were pure research since the hydrocarbon products could not compete with petroleum as fuels. However, due to wartime fuel shortages, Oriental countries, such as Japan and China, turned to vegetable oil fuels as petroleum substitutes. Much of this research was done hastily, and many of the details of these studies are incomplete or missing. [14]

Work was done in Japan in 1921 by both Kobayashi and Inouye. Kobayashi decomposed soybean oil, coconut oil, and stearic acid at temperatures of approximately 700 C to obtain "vegetable petroleum". The best yields resulted from using stearic acid. [15-17] Inouye, on the other hand, obtained similar results working



primarily on thermal cracking of the vegetable oil soaps. [18]

In 1922 Hirose and Yamada, also in Japan, performed pyrolysis on the sodium soaps of herring oil to obtain a 53 percent yield of a highly unsaturated oil containing no naphthenes. Excess methane was also reported. [19]

Gallo and Corelli in 1923 catalytically decomposed vegetable oils with superheated steam in the presence of alkaline earths and passed the vapors over a ferrous oxide catalyst at 550 C. Their hydrocarbon yields ranged from 60 to 65 percent, and had both paraffins and olefins in the liquid product. [20]

Also in 1923 Zelinski and Levine, working in the Soviet Union, studied the decomposition of some of the higher fatty acids. Little work on actual vegetable oil decarboxylation has been done in the USSR. [21]

The decomposition of cottonseed oil in a closed vessel at 450 C was studied by Waterman and Perquin in 1924. Liquid products consisted of a hydrocarbon mixture primarily in the gasoline boiling range. [22]

In the 1920's Sato and his co-workers in Japan investigated the dry distillation of calcium and magnesium soaps of soybean oil both at atmospheric and reduced pressure. At atmospheric pressure the constituents of the resulting liquid products were primarily paraffins, olefins, and naphthenes. They found that the magnesium soap decomposed at lower temperatures, and also gave heavier products than its calcium counterpart. Sato also pyrolyzed calcium and magnesium stearates and oleates under pressures of 5-7 mm Hg at 500 C. A substantial amount of ketones was produced along with various hydrocarbons. [23-27]

A process patented in Britain by Worsley (1932) described the decarboxylation of vegetable oils in the presence of activated carbon at 350 C. Hydrocarbon yields of 75 percent were obtained in the 110-250 C boiling range. [28]

Egloff, Morell, and Faragher in 1932 decarboxylated palm oil under pressures of 50 to 135 psi. Maximum liquid product yields were obtained at the lower pressures. [29] In another study, they pressure-cracked fish oil at 300-400 C and 60-100 psi. The gasoline range product yield increased and the diesel range products decreased with increasing pressure. [30] In the same year, Egloff and Morell cracked cottonseed oil under high pressure to obtain almost a 60 percent yield of products in the gasoline boiling range. [31] In a separate study, Egloff and Nelson obtained similar results from the cracking of seal oil. [32]

In China, during 1935 Ping decomposed nine different vegetable oils of various degrees of unsaturation with an aluminum chloride catalyst. He obtained primarily liquid products at distillation



temperatures above 250 C. The more saturated vegetable oils gave heavier products. [33,34]

In the same year, Koo and Cheng decarboxylated cottonseed, soybean, tung, and rapeseed oils using a sodium hydroxide catalyst at 800 F and no catalyst at 1000 F. Higher product yields were observed at the lower temperature using the catalyst. They were primarily interested in gasoline production. [35-37]

In 1939 Dalal and Mehta in India cracked vegetable oils by two different methods; they decomposed the liquid oils in iron and glass tubes, and also distilled the oils in the presence of a zinc chloride catalyst. They found that liquid product yields increased with increasing temperature and decreased with increasing unsaturation of the vegetable oil. [38]

The effect of the addition of lime to the reaction mixture on the cracking of tung oil was studied by Chang, Shiah, and Chan in 1941. They were primarily interested in gasoline product yields and found that the amount of lime had little effect on their yields. [39]

Ishakawa in a 1943 Japanese patent described the decomposition of stearic acid at 400 C for 3-5 hours in the presence of tin and lead. Primary products were heptadecene and heptadecane. [40]

A 1944 British patent by Worsley showed how to obtain hydrocarbon fuels by cracking vaporized vegetable oils at 500-650 C. [41]

Prior to and during World War II, decomposition of tung, soybean, peanut, cottonseed, and rapeseed oils was carried out in China by Chang and Wan. Various methods were used, including vapor-phase cracking, liquid-phase high pressure cracking, liquid-phase catalytic cracking, and soap pyrolysis. The best yields of liquid products were obtained with the liquid-phase catalytic process at temperatures of 300 to 350 C using aluminum chloride catalysts. [42]

In 1946 Goswami, Chakrabarty, and Modak, working in India, pyrolyzed oleic acid at about 350 C. A 50 percent hydrocarbon yield was obtained using a copper catalyst. [43]

A 1947 Japanese patent by Tokunaga described the catalytic pyrolysis of saturated fatty acids to olefins at temperatures of approximately 300 C. He used granular catalysts consisting of binary mixtures of silica gel, alumina, activated acidic clay, or bentonite with various metal oxides or hydroxides. [44]

Mandlekar and co-workers in 1947 pressure-distilled a number of vegetable oils in India. Diesel range products were found to decrease with increasing pressure with the highest yields obtained by cracking coconut oil at 45 psi. Also, diesel-range products



decreased with increasing zinc chloride catalyst. [45]

Petroff and Prats patented a process in 1948 for producing hydrocarbon fuels from the pyrolysis of the calcium soaps of coconut oil. Excess powdered slaked lime was added to the reaction mixture as a catalyst and temperatures up to 500 C were used. They claimed liquid product yields up to 97 percent with some gasoline, but the majority of the products were heavier oils. [46]

In 1948 Ishakawa and co-workers pyrolyzed stearic acid for 20 hours to obtain about a 70 percent yield of C10 to C15 olefins. [47]

Hsu, Osburn, and Grove in 1950 decarboxylated the calcium salts of both stearic acid and tung oil. Both soaps decomposed to give paraffinic and olefinic products. The liquid product yields were substantially higher for the calcium stearate. [48]

Tokunaga in 1950 studied the decarboxylation of palm, coconut, and chrysalis fatty acids using various mixed clay-metal oxide catalysts. He found that decomposition of fatty acids with higher degrees of unsaturation produced lower molecular weight hydrocarbons. [49]

In 1950 Toyoda obtained primarily a saturated hydrocarbon product by pyrolyzing the sodium salts of various fatty acids in the presence of a sodium hydroxide catalyst. [50]

Products from the decomposition of tung oil pyrolyzed in the presence of aluminum chloride at 450 C were separated into four fractions by Huang in 1951. These were a gasoline fraction, 60-200 C; a kerosene fraction, 200-275 C; a gas oil fraction, 275-350 C; and a lubricating oil fraction, above 350 C. [51]

Numerous others have investigated the thermal or catalytic cracking of vegetable oils or their calcium salts. Their experiments are similar to others mentioned above and will not be described in detail here. Their names, years of principal work and appropriate references are as follows: Melis-1924 [56], Oberhausen-1929 [57], Petrov-1931 [58], Delaby and Charonnat-1930 [59], Beuer et al.-1935 [60], Lo and Tsai-1936 [61-62], Bouffort-1939 [63], Lo-1940 [64], Arnoux-1941 [65], and Gomez-1942 [66].

#### Current Period

From the early 1950's until the late 1970's, little was done in the field of decarboxylation. Petroleum was plentiful and relatively inexpensive, and there was little incentive to produce fuels by alternative means. Following is a chronological summary of major decarboxylation experiments performed between 1978 and 1983.

A 1978 U.S. patent by Rao of India described the production of



hydrocarbons by thermolysis of vegetable oils at atmospheric pressure. The process involves liquid-phase decarboxylation in the presence of a silica-alumina catalyst impregnated with oxides of the transition metals. Reaction temperatures ranged from 300-700 C with yield up to 70 percent reported at 420 C. An increase in the liquid hourly space velocity of the vegetable oil feed also increased the liquid product yield to some extent. [52]

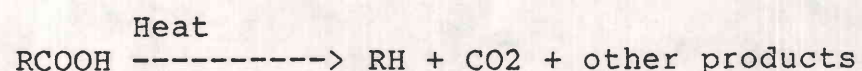
Weisz, Haag, and Rodewald in 1979 transformed various vegetable oils into a hydrocarbon fuel using shape-selective catalysis. They used a ZSM-5 zeolite catalyst to produce a high grade fuel in the gasoline range. The process involved initial thermal decomposition of the vegetable oils to smaller hydrocarbons followed by zeolite restructuring to the desired product. [53]

In 1982 Alencar, Alves, and Craveiro pyrolyzed native Brazilian vegetable oils without a catalyst at 300 C for four hours. The liquid product yield was about 50 percent and contained mostly paraffins and olefins. [54]

Another recent study in Brazil by Anjos, Gonzalez, Lam, and Frety was concerned with the production of diesel fuels from decomposition of soybean oil. Both crude and hydrogenated oils were vaporized and passed over either acidic or basic catalysts in glass tubular reactor at 300-500 C. The products from these experiments were analyzed by infrared spectroscopy and gas chromatography. Results from these experiments were compared with catalytic decomposition of stearic and oleic acids under similar conditions. It was found that the best liquid-product yields were obtained from the pyrolysis of the saturated oils. Also, decarboxylation of hydrogenated soybean oil gave fewer oxygen-containing products than decomposition of stearic acid. [55]

#### DECARBOXYLATION PROCESSES

The fatty acid components of all vegetable oils will, with sufficient heat, break down into constituent hydrocarbon and carbon dioxide groups according to the following simplified reaction:



A major problem with decarboxylation has been to find a "form" of the fatty acid suitable for cracking which involves the mildest (and presumably most economic) reaction conditions. Temperatures great enough to cause spontaneous decarboxylation of most fatty acids are usually well above their boiling points. Therefore, the cracking of pure vegetable oils without catalysts must either be done in the vapor phase or under sufficient pressure to cause the oils to remain liquid. Both of these approaches have various problems, which will be discussed later. Alternatives such as catalytic cracking or soap formation can lower the reaction temperature sufficiently to allow it to proceed in the liquid (or



solid) state. For these and other reasons, numerous cracking methods have been attempted; some successful enough to be implemented on a production scale.

Decarboxylation reactions of vegetable oils can be classified into four general categories:

1. Liquid-phase catalytic cracking
2. Liquid-phase high pressure cracking
3. Vapor-phase cracking
4. Soap pyrolysis

For all of the above processes either heat alone or heat in conjunction with catalysts is used. As would be expected, the addition of catalysts allows processing at lower temperatures. The major differences between these processes is the phase of the substance being cracked (gas, liquid, or solid).

Reforming operations have been used with vegetable oils in pyrolytic processes [53], but will not be discussed in detail here because they involve more than decarboxylation.

Following is a discussion of each of these major processes, giving approximate reaction conditions and typical yields.

#### Liquid-Phase Catalytic Cracking

More research effort has gone into studying direct decarboxylation of the raw vegetable oils in the liquid state than the other three processes. In this process the vegetable oil is heated to temperatures of 300-400 C in the presence of a catalyst. Certain oils have been cracked in the absence of catalysts with yields of about 50 percent, but this is unusual. [54] In much of the early work, unsophisticated catalysts were used with surprisingly good results.

In most studies pyrolysis of saturated vegetable oils gave more liquid products than decomposition of unsaturated oils. In one study liquid cottonseed oil and tung oil were decarboxylated using identical conditions. The more highly unsaturated tung oil had liquid-product yields of 75 percent compared with 82 percent for the cottonseed oil. [42]

Listed below are reaction temperatures and liquid-product yields for some of the liquid-phase catalytic cracking studies which have been done:



Year	Catalyst	Maximum Temperature	Yield	Ref.
1921	Various	400-450 C	--	5-13
1921	None	700	--	15-17
1932	Activated carbon	350 C	--	28
1935	Aluminum chloride	--	75%	33,34
1935	Sodium hydroxide	425	53	35-37
1943	Tin, Lead	400	--	40
1945	Aluminum chloride	--	--	14
1946	Copper	350-385	50	43
1947	Various	300-350	72-83	42
1947	Various	300	--	44
1950	Clay metal oxides	--	--	49
1951	Aluminum chloride	450	--	51
1978	Various	420-480	20-72	52
1982	None	300	50	54

#### Liquid-Phase High Pressure Cracking

In liquid-phase high pressure cracking the vegetable oil is heated to approximately 400-500 C under pressures of 50-300 psig. These high pressures are necessary to keep the oil in the liquid phase for a sufficient time to allow cracking without the aid of catalysts. Liquid product yields have typically ranged from 25-75 percent. This process has rarely been used because of the obvious problems associated with high pressure equipment. In addition, overall liquid product yields are usually lower for this process than for the others. [22,29-32,42,45]

#### Vapor-Phase Cracking

For vapor-phase cracking the liquid vegetable oil is heated to a sufficiently high temperature (300-600 C) to cause it to partially decompose. The vapors produced are passed over a catalyst where they are further decarboxylated. The cracked products are then condensed by cooling.

This process has not been used as much as some of the others for a number of reasons. The processing equipment is somewhat more expensive and the yields are usually lower than for the other processes. Typical yields for this process range from 30-65 percent.

Following are results from several vapor-phase cracking experiments, including catalyst used, reaction temperature and



liquid product yields obtained:

Year	Catalyst	Temperature	Yield	Ref.
1921	Various	400-450 C	--	5-13
1923	FeO	550	60-65%	20
1944	--	500-650	--	41
1947	None	400-450	55-56	42
1983	Silica-alumina	300-500	32-55	55

#### Soap Pyrolysis

In soap pyrolysis the fatty acids of the vegetable oils are converted into metal salts (soaps) prior to cracking at atmospheric pressure. Use of the soaps allows processing at reduced temperatures, usually under 400 C. According to one source, this process has historically occupied the leading position in total output of vegetable oil fuels. Soap cracking, however, has not experienced the recent popularity that liquid-phase catalytic cracking has.

In a patent describing the pyrolysis of calcium soaps, calcium hydroxide is recommended as a catalyst. In that study, liquid-product yields of up to 97 percent are claimed with about 70 percent of that being in the diesel range. The maximum temperature used for that particular reaction was 330 C. [46]

Again, as with liquid-phase cracking, the types of products formed by soap pyrolysis depend on the degree of unsaturation of the original oil used to make the soap. In a 1950 study, the soap of a saturated oil (stearic acid) gave liquid-product yields of 76 percent compared with 42 percent for pyrolysis of the soaps derived from the more unsaturated tung oil. [48]

The type of metal used to fabricate the soap is also important in the cracking operation. Calcium soaps have been used to a greater extent than other types because of their availability and low expense. Magnesium soaps, however, have been reported to decompose more rapidly and at lower temperatures than their calcium counterparts. [27] Sodium and potassium soaps have been avoided because of extensive foaming and greater expense. [14]

Listed below are several soap pyrolysis experiments that have been performed, complete with reaction temperatures and liquid-product yields:

Year	Temperature	Yield	Ref.
1920	550-600 C	60%	4
1922	--	53	19
1926	500	--	23-27
1945	--	55	14
1947	--	72-74	42
1948	330-500	97	46
1950	315-530	42-76	48



It has been reported that sodium and some other alkali soaps poison nickel hydrogenation catalysts. [73]

#### Mechanisms of Decarboxylation

Decarboxylation is a complex process about which little is understood. The situation is further complicated by the fact that the actual mechanism is dependent on many factors, including reaction temperatures and pressures, whether or not catalysts are used, and the type, form, and degree of unsaturation of the vegetable oil used.

To date, mechanisms of vegetable oil decarboxylation have not been studied extensively; instead research has concentrated on fatty acids. It is presumed that since triglycerides are partially composed of fatty acids, the mechanisms would be similar for both.

The thermal decomposition of saturated fatty acids has been presumed to proceed via the following mechanism: (1) dehydration to anhydrides, (2) decarboxylation to ketones, and (3) decarbonylation to paraffins and olefins. This sequence is supported by the fact that ketones are often produced by pyrolyzing fatty acids using milder conditions (temperature and pressure) than those used for hydrocarbon synthesis. [67]

Unsaturated fatty acids having, or capable of forming, alpha-beta or beta-gamma unsaturation may decarboxylate by an intermolecular process. Pyrolysis of these fatty acids usually gives terminal olefins at lower temperatures than is generally required for fatty acid decarboxylation. A number of investigations have indicated that the thermal decarboxylation of certain alpha-beta unsaturated fatty acids may proceed by the beta-gamma isomer as an intermediate. [68-70] These beta-gamma unsaturated fatty acids are thermally unstable and decarboxylate easily. Therefore, it appears that any unsaturated fatty acid whose double bond system is able to migrate to the beta-gamma position at high temperature will preferentially decarboxylate to a terminal olefin rather than undergo ketonic decarboxylation.

The thermal migration of double bonds during the pyrolysis of unsaturated fatty acids appears to be quite common. This helps explain the many different olefins formed by the decarboxylation of a single fatty acid.

The decarboxylation of fatty acid soaps has also been shown to proceed via ketone intermediates. This was first demonstrated by Sato in Japan working with calcium and magnesium stearates and oleates. [71] Hsu, Osburn and Grove postulated a similar mechanism for the pyrolysis of calcium stearate and tungate. [48]

The degree of unsaturation of the vegetable oil or associated soap has been shown to affect decarboxylation products. The



carbon-carbon double bond is a more active reaction site than the single bond. When this reaction site is eliminated by hydrogenation, the reactivity of the molecule shifts to other positions such as to the carboxyl group. Since the carboxyl group is at the end of the carbon chain, the decomposition of an oil without double bonds will result in a hydrocarbon of greater molecular weight than decomposition of an unsaturated oil.

The reason that the thermal decomposition of the free fatty acids produced more oxygen-containing liquids than decarboxylation of the hydrogenated vegetable oils is not clear. This particular finding has only been documented clearly in one study. They speculated that the size of the triglyceride molecule compared to the smaller fatty acid molecules might be influencing the reaction mechanism. [55]

#### SUMMARY

##### Decarboxylation

All of these processes had results that were similar. The liquid-phase catalytic process and the soap pyrolysis have definite advantages over both the vapor-phase cracking and liquid-phase pressure cracking. They allow processing at lower temperatures and pressures which is beneficial both in terms of equipment and operating costs and of course, safety. The most important factor, however, is that these two processes have been shown to consistently give higher yields of diesel-range products than the other two methods.

The cracking mechanism always results in paraffinic and olefinic products, no matter which process or which initial reactants are used. The cracked mixture also usually contains a mixture of a few naphthenic and aromatic products.

In studies where high pressure and atmospheric pressure cracking were compared, the high pressure process invariably gave lower yields of diesel-range products. In one study, cottonseed oil was cracked at 450 C and 280 psig with no catalyst; liquid-product yields were about 65 percent. At atmospheric pressure and 300 C using an aluminum chloride catalyst, yields were over 80 percent [42]

In general, higher processing temperatures also result in fewer diesel-range products. In a Brazilian study, soybean oil was cracked at various temperatures from 300 to 500 C, holding other conditions constant. The liquid products decreased approximately 4-5 percent for every 100 degree rise in temperature. [55]

##### Hydrogenation

According to data from the majority of studies done, the



degree of unsaturation of the raw vegetable oil used had an effect on the quantity and type of products formed, no matter which decarboxylation process was used. Decarboxylation of saturated oils produced more liquid products (less gaseous and solid) and the products that were formed had a higher average molecular weight (more diesel range products) than unsaturated oils. The exact reason for this is unknown, but seems to have something to do with the decarboxylation mechanisms which change with increasing unsaturation. Lighter products are apparently formed as the oils "crack" at the double bonds rather than at the carboxyl groups. This was not explored by many researchers, because they were usually attempting to maximize the gasoline-range products and extra cracking was desirable to some extent.

Saturation also seems to affect the characteristics of the decarboxylation products. A Brazilian study indicated that cracking of the pre-hydrogenated vegetable oils produced fewer oxygen-containing liquids than cracking of the free fatty acids. [55]

However, because some soaps tend to poison hydrogenation catalysts, it appears that, if soaps are to be used to produce diesel fuels, the vegetable oils should be saturated before converting them to soaps.

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To make this literature survey as complete as possible, some references were included even if they had not been reviewed for this study. Much of the early research was reported in foreign journals that are not readily available. Also, copies of some foreign references were obtained, but not translated. Therefore, in the following list, parentheses were placed behind the reference numbers to denote an article that had not been personally reviewed; the number inside the parentheses indicates the reviewed reference in which that particular article was discussed. If a copy of the article had been obtained but was in a foreign language, F was also included inside the parentheses.

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